CHEMISTRY IN MODERN LIFE

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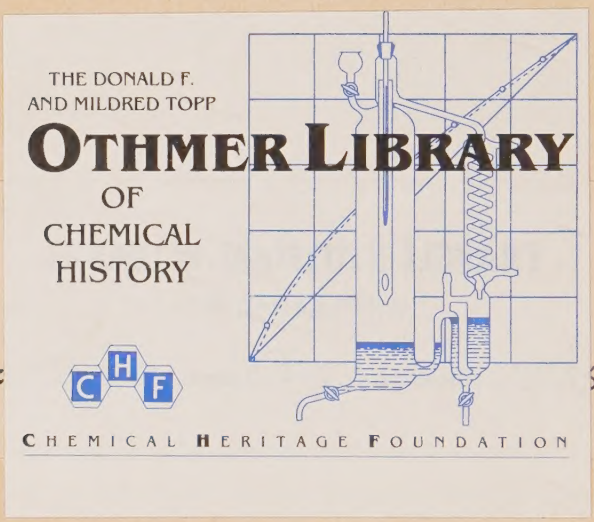
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CHEMISTRY IN MODERN LIFE

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A popular series treating their influence on the development of civilization

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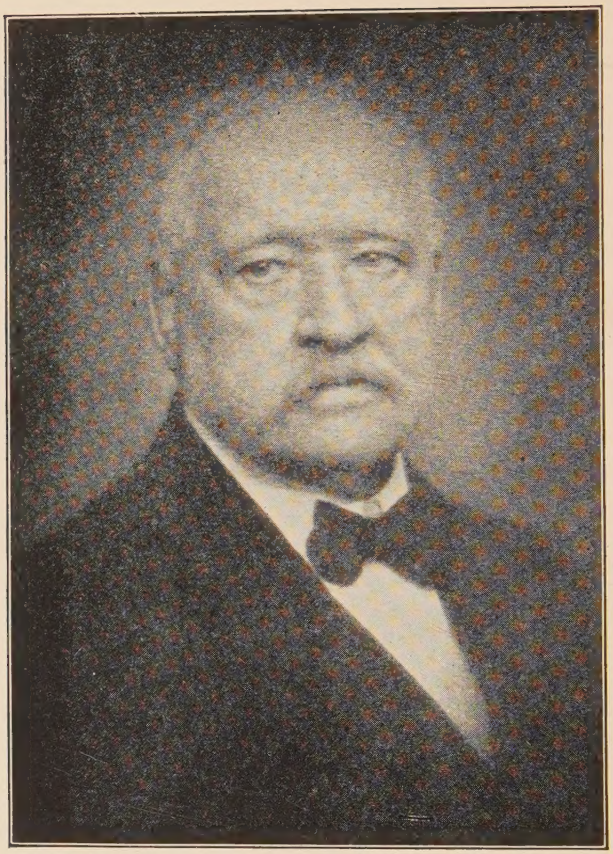

Frontispiece

SVANTE ARRHENIUS

Chemistry in Modern Life

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NEW YORK
D. VAN NOSTRAND COMPANY
EIGHT WARREN STREET
1925

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Sept 1925
Publ 3F previous ed.

PRINTED IN THE U. S. A. BY
THE PLIMPTON PRESS, NORWOOD, MASS.

AUTHOR'S PREFACE TO THE AMERICAN EDITION

Our age is often called the electric era, sometimes the era of paper. It would be more correct to call it the age of natural sciences, and especially of exact sciences. Physics and chemistry have revolutionized our daily life. It once seemed that physics was most important; for the wonders of electricity appeared more revolutionary than anything else. But on closer consideration we discover that chemistry has been of still greater importance in modern culture. This is because with the aid of chemistry we are able to transform rough raw materials of little or no value into products of extreme value. The most striking example of this is in the production of ammonia and nitric acid. In this case the raw materials are the constituents of air and water. They occur nearly everywhere that man exists, and therefore they have no value. But, for the preparation of the ammonia, and eventually of the nitric acid, a great source of energy is necessary, as well as the labor of men working in factories. The cost of the energy and of the labor, therefore, determine the price of the products. These products are of immense value in agriculture and for the making of explosives.

The bitter experience given us by the World War, and by the after-years of exigency demonstrated with hard fisted emphasis the necessity for chemical industry. So we see today how the nations are trying to develop this branch of science for the best possible improvement of their situation. The most practical way to repair the heavy losses caused by the war lies in the application of chemistry.

A most important question, which has caused much discussion in recent years, is the question of the sufficiency of

75153

supply of the raw materials which are used by chemical industry in immense quantities. Only in exceptional cases do these raw materials occur so abundantly that we need have no fear of their eventual exhaustion. Even America, today the land most blessed with natural riches, may use up many of them within a few centuries. Of the ores of the heavy metals, it must be stated that they occur only in very limited quantities. The better iron ores are being worked rapidly, because of their great demand for industrial purposes. But it must be confessed that we have a great abundance of low-grade iron ores, which must be attacked after the exhaustion of the more valuable ores, perhaps in about 1,000 years at most. Furthermore for many purposes we may use the light metals, such as aluminium, at hand in unexhaustible quantities in bauxite and as a constituent of clay, in place of the heavy ones.

Far greater is the danger regarding the energy necessary for chemical operations. The material basis of our present civilization depends on the use of fossil fuel, chiefly coal and petroleum. In earlier periods of history one generation of men lived very nearly as did the preceding one. Centuries were necessary to produce great changes in the conditions of life. This circumstance has been completely altered by the use of fossil fuel, for the development has taken on an explosive character. During the last century as much coal was consumed in each ten years as had been used in the whole preceding time. The conditions for the consumption of iron and most other metals, of petroleum, and of other necessities such as paper, glass, etc., have been similar. The recent war, which marks a great retrogression in civilization, has diminished this rate of progress for a time. But it has been calculated that the accessible fossil coals will be nearly at an end in about 1,000 years, and petroleum in about twenty years. If we do not find some new source of energy within a thousand years, humanity will fall back to a state of civilization similar to that about a century ago, while the number of inhabitants of our planet will have to diminish to a corresponding degree. Luckily we

have the energy of the water-falls which will not diminish in a sensible degree in comprehensible time, unless we cut off the forests on which the water reserve is more or less dependent. We must harness these falls to save as much as possible of our present material culture. But even when we have taken them into our service they cannot compensate for the loss of fossil fuels. Humanity stands, therefore, before a great problem of finding new raw materials and new sources of energy that shall never become exhausted. In the meantime we must not waste what we have, but must leave as much as possible for coming generations.

Doubtless humanity will succeed eventually in solving this problem, at least partially. But when the new resources have been found the hearth of civilization will move to the places of their chief occurrence, and the life-conditions of mankind may undergo a great revolution.

THE AUTHOR

STOCKHOLM,
August, 1923.

TRANSLATOR'S PREFACE

HERE in America we sit back and beam about us on a land of plenty and resource. Of course we are bothered by a few petty details — next winter's coal — the cost of electric power for that new factory project — or the rising cost of construction steel, but we lay these evils upon the miner, or the service company, or the steel trust, and continue our serene way.

Do we ever stop to think, "How long can this go on?" Not often. Do we ever stop to consider how much this luxurious, comfortable life we live depends on "material culture," on the development of glass and pottery, on metallurgy, on fossil fuel, on rubber and cellulose, on nitrate and coal tar? The present generation was born to the inheritance of these things. We have no memory of days when these were not. We seem to display no ambition to look whence these things come, nor to look into a future in which perhaps we shall not have them.

Yet days of want for some of the "necessities" are close at hand. American oil in *twenty years*, the world supply of coal perhaps in 1000 years, at a very little above the present rate of consumption! In terms of history the latter period is but a moment longer than the former. Iron increasingly scarce, or obtainable only from poorer and poorer ores with consequent increasing cost. The Age of Heavy Metals dwindles! America can be a little more smug than can Europe in these matters. Iron and coal will last us for a while, if we hoard them, but not if we supply the world; yet such an appeal may come to us shortly.

Our ideal culture, our luxury, our home-life, our urban civilization and our fundamental outlook on life may go overboard all in one great wave, if our material culture, upon which all else is based, and without which these things cannot exist,

is to fail us. We have lived upon our principal, we have thrown to the winds our fuel, we have cut down our forests and refused to reforest, careless of the waterpower that is dependent upon them.

The answer is Conservation, — frugal housekeeping before it is too late and substitution where it is possible today. Concrete construction has already begun to lessen the use of steel construction, water powers are substituting coal, though this is not everywhere possible; but more can be done in these fields and in many others. We can reforest — develop our waterpower — economize with the treasures of nature. Coal can be burned at or near the mines to make electricity, and so energy can be transported more efficiently via copper cables then when half the energy (as coal) must be used to haul the rest by railway. Let the government take control, if necessary. Where will our fine development of aviation be, should liquid fuel give out? A launching into the air — a bitter landing for lack of what might have been conserved to this end. Alcohol for motor fuel, you say? There are no definite signs today that it ever will be practical on the scale of our present use of petroleum. Atomic energy, you say? A chimera today — possible, yes, after centuries more of study — or perhaps never. We cannot keep house on the hope that some one will die and leave us a million dollars, nor can we on the chance that atomic energy can safely be unlocked.

Scientists over the earth are concerned in study of these dangers — yet they see no way out save conservation. Thou Shalt Not Waste! We are faced by the "Chemist's Commandment" at every turn of our modern civilization.

Here in substance is the message of this book by Svante Arrhenius, chemist, cosmist, teacher, director of the Nobel Institute, president of the Swedish American Foundation (Sverige Amerika Stiftelsen). From the outermost star to the interior of the atom his searching mind has roamed to find the riddle of the future. Yet the horizons that he sees are dark ones unless we are civilized enough to mend our

ways, unless today we take to the game of conservation, now that the frontiers of the earth are gone, as once we took to pioneering.

Professor Arrhenius continues the succession of brilliant names which Sweden has supplied to science, name like Scheele, Linnaeus and Berzelius. The name of Svante Arrhenius is inseparably connected with one of the most important of chemical theories — the theory of electrolytic dissociation. An estimate from the pen of another expert in his field, of the importance of Arrhenius' theory is given by Professor Charles Kraus of Clark University, in his book on the "Properties of Electrically Conducting Systems." "It is to Arrhenius that is due the credit of first having developed a theory of electrolytes quantitative in its nature, the correctness of which it was possible to determine by exact quantitative methods."

To the writer, as a student on the American Scandinavian Foundation, the stimulus of Professor Arrhenius was immense; his interest in the relation of material culture to world affairs, his cosmics, as well as his intricately detailed chemical studies, such as those in the kinetics of immunochemistry — all these, combined with a genial, kindly personality, led to many visits to his home and workshop, the Nobel Laboratory outside Stockholm.

The New Chemistry, the theories of the inner atom and crystal structures, the chemistries of Bohr, Bragg, Moseley, Thompson, Rutherford and Langmuir, receive little mention in this book. These in a sense are but the unborn concepts of the future. They have produced but few effects upon our life. True the chemistry of the vacuum tube gives us radio-broadcasting. Perhaps the nineteen-twenties will come to be known as the transitional decade of the new chemistry and physics. But, outside the field of radiation physics, these have as yet given but slight service to civilization, so they can scarcely be looked upon as more than a shadow of the future across our modern life.

Thanks are due to Dr. Edwin E. Slosson of Science Service,

to Dr. F. W. Lane of the Bureau of Mines, for petroleum data, and to Dr. Ralph Hixon, and Miss Pauline H. Leonard.

Contributed illustrations are acknowledged from Professor Edgar F. Smith, Miss E. A. Wade, curator of the Springfield Museum of Art, Mr. Albert Demmler of the Vanadium Corporation, and from the E. I. duPont de Nemours Co., and the Aluminium Company of America.

C. S. L.

New Haven,
April, 1925.

CONTENTS

CHAPTER		PAGE
I.	Ancient Ideas About the Constitution of Matter	1
II.	The Ground-work of Scientific Chemistry	17
III.	Fire, Oxidation and Reduction	37
IV.	Tools and Metals	59
V.	The Cultural Value of Silica	85
VI.	The Chemistry of the Earth's Crust	111
VII.	Ores and Fossil Fuels	127
VIII.	The Chemistry of Water and Air	144
IX.	Sources of Energy	160
X.	Electricity and Chemistry	175
XI.	The Course of a Chemical Process	195
XII.	Dyes, Perfumes and Drugs	213
XIII.	Cellulose and Rubber	237
XIV.	Chemistry and the Bread Question	251
XV.	Housekeeping with the Treasures of Nature	267
	Index	277

ILLUSTRATIONS

FIGURES IN TEXT

FIGURE		PAGE
1.	Drilling Fire	37
2.	Bowing Fire	38
3.	Rubbing Fire	38
4.	Flinting Fire	39
5.	Döbereiner's Fire-lighter	41
6.	Pneumatic Timber Box	41
7.	Chemical Lighter	42
8.	Blowing Smoke Rings with Phosphine	47
9.	Surface Combustion Plate	49
10.	Surface Combustion Crucible Furnace	49
11.	Surface Combustion Boiler	50
12.	Early Work with Edged Tools	59
13.	Carvings on Reindeer Horn	60
14.	Later-Stone-Age Bowl	85
15.	Finger-mark Ornaments on Pottery	86
16.	Stone-Age Urn	86
17.	A Present Day Laboratory of Nature	152
18.	John Ericsson's Solar-engine	169
19.	Apparatus for Demonstrating the Migration of Ions	180
20.	The Daniell Cell	185

PLATES

PLATE		FACING PAGE
	Svante Arrhenius, (*Frontispiece*)	*Title-page*
I.	An Alchemist's Laboratory	12
II.	The Workshop of the Age of Heavy Metals	64
III.	An Alloy Steel Workshop	72
IV.	The Culture-Chemistry of Art Bronze	74
V.	In the Workshop of the Age of Light Metals	82
VI.	The Culture-Chemistry of Silica I	88
VII.	The Culture-Chemistry of Silica II	96
VIII.	The Culture-Chemistry of Silica III	102
IX.	The Roosevelt Dam	168
X.	The Comfort-Chemistry of Cellulose	244
XI.	Collecting Rubber Latex	248

Chemistry in Modern Life

Chapter I

ANCIENT IDEAS ABOUT THE CONSTITUTION OF MATTER

We commonly fancy that the most ancient folk of whom we have any knowledge held the belief that matter could be destroyed and likewise could appear out of nothing through a sort of act of creation. This belief we first find, however, among people who have come very far, and, let us here add, entirely too far, in ability to think abstractly. The idea appears in the Indian *Vedas* (1500–1000 B.C.) yet it was never developed entirely logically, for even before the world's existence an all-pervading uniform solution was supposed to exist, which solution was made visible by God (Brahma) with the aid of the five elements. Afterwards, the act of creation came to pass as a result of Brahma's will. The creation resulted in annihilation which again resulted in a new creation, and so on. This oscillating process, however, appeared principally to have applied to the living beings and not so much to the matter itself.

Far simpler is Zarathustra's (Zoroaster's) teaching according to which the light god, Ormuzd, who was the unformed matter which like a chaos filled infinite space, formed out of several god-entities and heavenly spaces the following things in the order given:

1. The heavenly bodies: sun, moon and stars.
2. Fire.
3. Water.
4. Earth and the living beings.

Here one finds a division which corresponds to the later four

elements. Previously the Indians had introduced a fifth, "Air," while the first, the celestial element, dropped out or was accounted equivalent to "Fire."

Just as in Zarathustra's doctrine one finds among all primitive people the notion regarding the world's primordial state that, until a "beginning," there pre-existed unordered matter, commonly called "Chaos," which was changed to the different natural objects by a divine being. The doctrine of the indestructibility of matter in later times, since man made use of the balance to measure mass, has expanded into one of the basic principles of modern science which says that matter's mass is unchangeable — it can never increase or decrease.

After this first occurrence we also find the doctrine of the four different elements in the oriental countries, in Babylon as well as in Persia and India. Perhaps the Greek philosophers got their ideas about the elements from the Orient. From the first there existed among the Greeks a tendency to simplification in that one of the elements was claimed to be the most important primitive material out of which the other elements could be regarded as taking their origin. Thus, Thales claimed the water, Anaximenes, the air, and Heraklitus, the fire, as the most primitive. Finally, it came about that Empedocles (who lived about 500 B.C.) took all four elements to be equal — that is to say, besides the three last named, also earth. This teaching was taken up by Aristotle and prevailed, protected by Aristotle's enormous authority till long afterward in modern times.

In this very simple theory the ancients summarized their observations of the outer world. Indeed, these were very insignificant. Three of the fundamental elements — air, water and earth — constituted the three fixed states in which matter appeared — the gas form, the fluid and the solid. This knowledge belonged not to the science which we now call chemistry, but rather to that which we as well as the ancients call physics. The fourth element, fire, constituted the shining material which we observe in the celestial bodies and which

also appears among strongly heated earthly objects. We now know that the same body can appear in the three different states, the commonest example being water which is fluid, but which can be changed to a solid form, for on cooling it goes over into ice, or to a gas form, since it is transformed to steam through the application of heat. Even the ancient world had an inkling of this fact. Plato said in *Timaios*, "Fire is burning air. Condense and quench this, one gets back air; the air (water-vapor) again condenses to a cloud and fog, which by running together gives fluid water. From the water finally stones and earth form by condensation." This last manifestation refers not to ice formation but to the settling out from impure water of suspended solid particles or the dissolved salts. Plato's observation was consequently quite imperfect and superficial. This characteristically accounts for the philosophical tendencies prevailing among the ancients, for they satisfied themselves with unclear generalizations in place of careful observations. Experimental research was almost wholly disregarded in the ancient world.

In Plato's doctrine condensation was by far the most important factor. Air condensed to cloud and fog, this again to water, which again condensed to earth and stones. Even when fire changed to air there occurred a condensation of space, said Plato. The desire to draw a general conclusion had set the great philosopher on the wrong road. Beyond doubt, a condensation occurs when water vapor changes to the liquid form. But as we well know an increase of volume occurs when water freezes. This was unknown to Plato (428–347 B.C.) just as he did not know that water differs in this particular from the great majority of fluids. The notion of density or specific gravity was first clearly set forth by Archimedes (287–212 B.C.). Only by employing general, unconfirmed notions could the Platonic doctrines about elements be accepted and win popularity.

With regard to the relationship of fire to air it is well known that air becomes warmer when it is compressed, a property

which is made use of in the pneumatic tinderbox for the production of fire. Had Plato known of that fact he would hardly have formulated his conceptions about fire and air as he did in *Timaios*.

With the three physical states of Plato and his wrong conception of density as a basis for generalization, his great pupil Aristotle (385–323 B.C.) turned his attention to the importance of heating and drying in nature. In themselves heat and humidity are of the greatest importance for the growth of organisms, and so for man's existence. Drying destroys vegetable growth and changes tillable fields to desert. Cold, which is to say the absence of heat, also hinders the growth of plants, and especially the maturing of their fruit. Aristotle introduced this concept into the definition of the four elements, explaining that warmth and coldness, humidity and dryness, are four fundamental sensations, and he achieved thus the following schematic representation:

Cold and dryness.....Earth
Heat and dryness .....Fire
Heat and moisture .....Air
Cold and moisture .....Water

More combinations than these are not to be thought of. Therefore, more than four elements cannot exist. That line of thought is always characteristic of the Platonic-Aristotelean philosophy, which unfortunately ruled the habits of thought for about two thousand years and even in our day strongly persists except in the domains of natural science. How wrong it is may be seen from the fact that air, as ordinary observation teaches, can be either cold or warm and equally may be dry or again moist, namely when it contains water vapor. All gradations may be found between these extremes. Nevertheless, schematic simplicity triumphed over doubts grounded upon observation, and the Aristotelean system solidified in a dry dogma which pinioned the wings of science in its growth.

Somewhat before Plato's time there lived in Abdera in Thrace the greatest truly scientific thinker of ancient times, Democritus

(born 460 B.C.). He had made clear to himself that water vapor and water ought not to be characterized as different elements since they really could change over into one another. There must be something common to them both. The very smallest parts in water and water vapor must be the same, only they lay further apart from one another in water vapor and therefore took up greater space than in the liquid water. Observations show us that these tiny parts are invisible. In order to understand why the transformation of water to water vapor (and vice versa) could always be accomplished, it was most logical and simplest to believe that the characteristic small parts were indestructible. Democritus assumed that these tiny parts were not further divisible — he, therefore, called them *atoms* (Greek for *indivisible*) — and he assumed that they were engaged in a perpetual motion. Through union of the atoms in different ways arose the different bodies that we find in nature. The indestructibility of matter had already been postulated by Empedocles, who claimed that all phenomena in the world depended on changes of form and of composition within bodies. Democritus did not let himself be bound to the postulation of four elements. He was powerfully opposed by Aristotle and his school and most of what we know about Democritus is taken from the critique of his teaching by the dominant school.

It is quite remarkable that, through the entire Middle Ages and down to the seventeenth century, no noteworthy advance was made in the teachings about the composition of substances. The chemists occupied themselves above all with the problem of the properties of metals. These seemed to them to be all of one nature and therefore they thought it should be possible to change one metal into another. They sought, therefore, to prepare the most valuable of all metals — namely, gold, out of less precious metals. They imagined that it should be possible to bring this about by some sort of color change. They knew that copper can be colored silver-white by treatment with arsenic compounds and that it takes on a gold color through treat-

ment with *calamine* (zinc carbonate). As we now well know, these changes depend upon the fact that this treatment forms in the one case a white alloy of copper and arsenic, in the other case a golden-yellow alloy of copper and zinc (brass). It had been known since ancient times that copper took on valuable properties by the addition of tin, forming the alloy bronze, notable for its hardness. Therefore, it seemed natural that they should be able to prepare gold and silver out of copper and other less precious metals by suitable additions. This concept was embodied in a theory that all metals contained a common ingredient called quicksilver because it was supposed to occur least-alloyed in the liquid metal, (mercury).

In the Orient, chemistry did not need, perforce, to grow into gold manufacturing. According to Berthelot it took that odd trend from Egypt. The Egyptian goldsmiths, for the purpose of forgery, prepared gold or silver-like alloys out of unprecious metals by which means they became very rich. The Greeks learned from the Egyptians this art of "transmutation" (changing metals into one another); from the Greeks, the Arabs learned, and finally from these latter the medieval Europeans took up the art. If one were to believe with Roger Bacon that a few grams of the philosopher's stone would have power to change a ton of base metal to gold, one would be greatly tempted to seek a fortune in the "Greek Art," as the transmutation of metals to gold was called. That art, then, which made up alchemy's chief aim, originated in Egypt.

The state of things in the Orient was quite different. There chemistry developed as a sort of auxiliary science to medicine, which was practiced after the beginning of our Christian Era in the Buddhistic monasteries, for it was the duty of the priests dwelling in them to cure all sorts of suffering, spiritual as well as corporeal. In such a monastery was to be found a great hospital. They believed that not solely a specific compound, but also the utterance of specific religious formulae were necessary to the physician's healing power. Thus chemistry took on a religious impress. The oldest Hindu writing about medicines

is found in one of the Veda-books, Atharva-Veda. Gold was considered as a sort of life elixir, lead as an agent for fighting magic. Pearls served as amulets to protect against sickness and to give one hundred years of life. Most drugs were of organic origin and only a few inorganic drugs were used, such as occur as natural products. Praphulla Chandra Ray who has written a history of Hindu chemistry notes that long before Hippocrates, the Indians developed a humoral-pathology and that it is more or less likely that the Indian teachings influenced the concepts of the Greeks. Little by little medicines of inorganic nature became commoner and they learned to prepare these with ability, especially the sulphur compounds of the metals. Quicksilver again came to take a central place. "It is only quicksilver which can make the body resistant and immortal," they said. Black mercuric sulphide was next believed in as a universal agent which ought to be compounded in all medicines. Mercury preparations were used against leprosy and other skin diseases and very likely the Arabs learned of this medium in India. Even lye, and caustic alkali prepared from it, played an important role. When the alkali acted too strongly they neutralized it with vinegar (acetic acid).

A clear account of the differences between the Occidental and the Oriental science was given by the Arab, Alberuni, (died 1039 A.D.) who visited India from 1017–1030 A.D. "The Hindus," he said, "do not care very much about alchemy, but no nation is a complete stranger to this science. . . . Adepts in the science seek to keep it secret and will not associate with any but their colleagues. Therefore, I could get enlightenment from the Hindus neither about what methods they employ in the science, nor as to what raw material they chiefly employ — mineral, animal or vegetable. I heard them talk only of sublimation, calcining and analysis, and also of 'swelling' talc, which in their speech is called 'talaka'; and therefore I surmise that they interest themselves in the mineral side of alchemy.

"They have a science which is similar to alchemy but is

peculiarly their own. They call it 'Rasayana,' a word derived fom 'rasa,' which means gold." [Ray notes here that in the older works "rasayana" meant a medicine which prolonged life, a sort of life elixir. Later, rasayana served to indicate the therapeutic use of mercury and even of other metals]. "An art was understood thereby which employed certain methods, drugs and mixed medicines, in large part obtained from the vegetable kingdom. This art restored health to the sick and youth to the aged. Mankind's life span in that world was stretched out to a great length."

This is a plain identification of Hindu chemistry with the so-called iatrochemistry (i.e. medical chemistry), which made its entrance into Europe half a thousand years later through the work of Paracelsus (1493–1541) and his followers. Among these one may name the German, Libavius (died 1616), who discovered tin chloride and described a method for the preparation of sulphuric acid which corresponded in principle with a method still in use; further, the Dutchman, van Helmont (1577–1644), who described carbon dioxide, which is obtained by fermentation, or from chalk or lye with acids and which even forms in animal bodies and in the earth. To this notable man we shall later return. The German, Francis de la Boe Sylvius (1614–1672), investigated combustion, respiration and phenomena of similar nature. He knew the difference between venous and arterial blood and that the clear red color of the latter depended upon the action of air. In England, Willis (1621–1675) disseminated the teachings of the iatrochemists. "The greatest scientific merit of 'iatrochemistry,' says Thorpe, "was that it made chemistry into a professional science as a result of which a great number of people studied it, and many new chemical compounds were discovered. Furthermore, everybody became more familiar with chemical phenomena so that need for a general theory to explain them became known. The next period strove to fulfill that need."

In the iatrochemist's time, three men stand out who worked

in applied chemistry, namely, Georg Agricola (1494–1555), father of metallurgy, who wrote the chief technical work of his century; Palissy (1510-1589), who laid the groundwork of rational ceramics; and Johann Rudolph Glauber (1604–1668), the greatest chemist of the time. The latter prepared hydrochloric acid and nitric acid, while after him is named Glauber's salt (sodium sulphate), a discovery which had extraordinarily great medical importance. Furthermore, he learned how to recognize many chlorides such as sal ammoniac, zinc chloride, arsenic and copper chlorides, and he seems to have made some studies with chlorine gas. Beyond this he was distinguished in niter and glass manufacture and in the preparation of new pigments. Also he wrote a handbook about chemical processes which became the model for similar works over a long period. In that period the chemists learned how to recognize a great number of inorganic salts. In the field of organic chemistry they discovered various salts of acetic acid, of tartaric acid, (among these tartar emetic), and of stearic acid, succinic acid and benzoic acid.

Since iatrochemistry flourished in Europe many hundreds of years after it had been developed to a high degree in India, one may well ask himself the question whether the ideas of Paracelsus did not originate in India. Ray claims that this was the case. The Califs, Harun (died 809 A.D.), and Mansur (died 1002), facilitated the translation of the most important Hindu works on medicine and pharmacy for the libraries of Bagdad and Cordova. An Indian doctor, Mankh, cured Harun-al-Raschid of a serious illness, translated one of the most important chemical treatises of Indian origin into Arabic, and wrote in that tongue a work upon the Indian medical plants. A great number of Mohammedan students went to India to acquire learning. Many Hindu doctors were summoned to the calif's court. The science of that time was practiced mainly in the Mohammedan world and from that world, especially from the Spanish Mohammedans, the knowledge was derived which gradually spread to the Occidental lands.

It is, therefore, not at all unlikely that iatrochemisty in Europe was introduced from India by way of the Arabs. It is wholly beyond doubt that Hindu chemistry was in touch with that of China. Chinese medical chemistry appears to antedate that of India for a pharmacopœia, or compendium of drugs is known which was compiled at a very early date (attributed to Shen-Nung about 2600 B.C.). Even in China chemistry had a medical and religious tint and its chief task apparently was to furnish a life elixir. At first they searched for this in the vegetable kingdom. Thus it is related that the Emperor Tschi-Hoang-Ti (about 218 B.C.) sent out various expeditions to places where it was hoped to find plants, from the juices of which a life elixir might be prepared. In the fourth century, a chemist, Ko-Hung, prepared a beverage cooked from cinnabar, a decoction presumed to "bestow upon mankind both a long life and an immortal soul." For the same purpose one could also use the sulfur-arsenic minerals, realgar and orpiment. To prepare the life elixir one ought to undergo a fast and ablutions and perform the work on a high mountain as near as possible to heaven. As these minerals are all powerful poisons we can well believe that not less than four emperors of the Tang dynasty were risking their lives when they tested the life elixir.

That chemistry in China was in close touch with that of India is quite natural, since the science was in the closest relationship to religion, and Buddhism was originally introduced into China from India, running an overwhelming course there in the seventh century. Countless Chinese priests visited India to study the holy doctrines. That chemical knowledge could have been transferred from India to the Occidental countries was demonstrated by Ray in the citation that the so-called Arabic numerals came to us from India through Arabic mediation. Similarly, the fables of La Fontaine came in part from India, in that they were translated from Sanscrit to Pahlavi [the speech of the Persian Dravidians], from that to Arabic, from that back into Persian and finally gave material for the French text.

Before the year 1600 the Western chemistry had far outstripped the Indian so that, contrary-wise, knowledge of chemistry went from Europe to India. The alchemists, who particularly occupied themselves with the transmutation of metals, as well as the iatrochemists who used chemistry in the service of medicine, and those chemists who were occupied with metallurgical and other industrial arts, had discovered a great number of new bodies, for the most part acids, bases and salts. Most of these were water soluble and were thought, therefore, to contain a common constituent called "salt." The insoluble bodies were believed similarly to contain a common constituent called "earth." But, besides these, there were found a number of substances like sulfur, oils and fatty substances which did not dissolve in water and which unlike earth were burnable. These were believed to contain a common constituent which was called "sulfur." They had, therefore, besides the old Aristotelean elements, new bodies, often called principles, which included the metallic principle — "quicksilver," as well as "salt" and "sulfur." The insoluble principle was the well known element of the ancients, "earth."

These opinions ruled long into the new age in spite of more rational beliefs which were repeatedly affirmed. Thus one can find the following conclusions in a text on chemistry which was published in 1712 by Urban Hjärne, director of a Swedish state laboratory. This first Swedish textbook of chemistry may be considered as a good survey of the beliefs about chemistry prevailing at that time.

Hjärne (1641–1724) wrote first of the four Aristotelean elements, of which all bodies were put together. Among these fire was the foremost; it was also called the divine element. Fire, which was found in the sun in purest form, was the origin of all things. Hjärne was very wroth against the distinguished Dutch chemist, van Helmont (1577–1644), who dared maintain that fire was no substance at all. Indeed, van Helmont said, "Flame is only the illuminated, and thus shining, smoke, which is a fatty vapor." The sun and stars sent out fire and the sun

got back just as much fire as it sent. (That last queer idea is found again in the beliefs of the great French naturalist, Buffon). A part of the sun's fire fell down on the planets and the moons and combined with their particles to form exhalations, which filled the firmament, and the fire also came to the earth where it strongly affected the health of mankind and the animals. One sees here the influence of the then dominant astrologers upon the trend of thought. The exhalations were also taken up by various bodies, especially by "quicksilver." Air was necessary for life and for combustion, as Boyle observed by research made in a vessel out of which the air was removed with the aid of a pump. Coal heated to glowing in such a vessel by means of a burning glass did not burn. Air pressure forced up water into the vessels of plants and, similarly, into springs in the earth. Water and earth were most passive elements — a view-point expressed by Hjärne as well as by the apothecary Lemery in Paris, who wrote the most esteemed textbook in chemistry of the period. Water entered to a greater extent into bodies than the other elements. For this reason one can understand why various philosophers, such as Thales, and van Helmont, expressed the opinion that water was the origin of everything.

Through combination of the four elements in different proportions the three principles were formed — quicksilver, salt and sulfur — which were constituents of all bodies. Among the salts, "the sour salt," (acid), was particularly important. An acid called "the universal sour salt," (sal acidum universale), arose from the innermost heated parts of the earth; it seems to have been identical with the "spiritus sali" of Paracelsus, (hydrochloric acid). When this acid encountered mineral oil it formed sulfur thereof, with shales it gave coal, with metals containing sulfur it gave vitriols, (salts of sulfuric acid with metals); together with fire from the sun and exhalations from the moon and the planets and combined with earth in sea water it was said to give acid-sea-salt.

Next Hjärne discussed the alkalies, both the volatile (ammo-

PLATE I

Courtesy of Professor Edgar F. Smith

AN ALCHEMIST'S LABORATORY

nia), and the two "fixed" alkalies (i.e. the non-volatile), namely, potash and soda. These latter were distinguished by the fact that they effervesced when mixed with an acid, (one can realize that the "alkalies" in quesion had taken up carbon dioxide out of the air). Common salt, (cooking salt or sodium chloride), contained as we may understand from its mode of preparation, a *whole train* of other substances, both acids and alkalies, fixed and volatile; furthermore, it contained water, fire, earth, and in less degree fat (which counted as sulfur). From this we can form an opinion of the degree of purity of the chemical preparations of the period. "When salt was dissolved in water and was boiled repeatedly, then the fire, and with it the salt content, went out of the salt." This conception arose without doubt from the observation that when one evaporated sea water by boiling, common salt crystallized out, and at the end, after the common salt, there came out other salts which are dissolved in sea water and which do not give the taste of common salt. After describing the above Hjärne listed a few other salts, among which the most important was saltpeter. These differed somewhat in composition from common salt. Thus, for example, the saltpeter contained much air, on which account an especially great expansion occurred when it decomposed, as in the ignition of gunpowder into which saltpeter entered as the essential component.

The two remaining principles, quicksilver and sulfur, were of far less importance than the salts. Therefore, Hjärne passed on to a much more important subject, that of solution and its opposite, precipitation. Solvents were divided into three classes, the salt type, the sulfur type, and the water type. Among the salty solvents, acids were the most important. They were able to dissolve metals, and limelike and earthy materials, as well as "darker" stones. Hjärne here had the sense not to uphold Lemery's claim that the particles of the solvent had points, for which the taste of the acids gave cause, and which pushed in between the particles of the body which dissolved and thereby broke apart the attachment between the latter

particles. Even the alkalies were solvents, for they dissolved the volatile constituents of fats, resins and other combustible materials.

To the sulfur type of solvent belonged pressed or distilled oils, such as olive oil, turpentine, and above all alcohol. These dissolved oily and resinous materials. The water type of solvents were: spring water, dew, rain water, snow water, sea water, distilled water, milk and beer. From this list it may be seen how materials were classified both by their source and preparation and their content of impurities. These watery solvents took up only the different salts, such as acids, alkalies, alum-bodies, vitriols and other neutral salts, also sugar, gums and mucilaginous materials.

Precipitation was caused by the opposites of the solvents. If a body was dissolved, for example, in alkali, then it precipitated on addition of acids which were the opposites of alkalies. Water was an opposite of fat; therefore, bodies which were dissolved in oil or spirit, often precipitated by addition of water to their solution. Furthermore, there were listed a number of specific precipitants such as silver nitrate which "precipitated" common salt.

Hjärne's doctrines, which seem so naïve to us, were similar to nearly all chemical theory at the beginning of the eighteenth century. With reference to combustion, Hjärne disclosed particularly uncertain beliefs. Air was necessary for combustion — hence it was supposed that air which rushed to the burning body, spread itself around the burning particles so that these became available to the fire. He contested the opinion, quite common even then, that the fire-flames only consisted of glowing particles, which rose in the air.

It may seem strange in our time that scientific men of that period should insist, for example, that all burnable materials such as olive oil contained sulfur, yet on no occasion did they try, (by *analysis*), to liberate sulfur from it; nor by combining sulfur with other bodies, (synthesis), try to prepare olive oil. The great lack of experimental knowledge was made up for by

rather arbitrary concepts which claimed to be philosophical and which were handled in a particularly careless manner. Weakness in demonstration was covered by the use of a verbosity which completely perplexed readers of chemical works. At times they insisted that the sulfur which was supposed to enter into the composition of olive oil, for example, was not at all the same as common sulfur, and in contradistinction it was called "philosophic sulfur." But in the next moment they forgot this difference and argued about the philosophic sulfur as if it were common sulfur. A similar amusing conception was Hjärne's belief about the universal acid, "sal acid universale," which was supposed to rise up out of the center of the earth and is presumed to be the same as hydrochloric acid. It is not improbable that the origin of this belief was grounded upon the fact that various acidic vapors do issue from crevices in the crust of the earth in volcanic regions. These vapors at times contain hydrochloric acid, but more commonly consist of hydrogen sulfide, and sulfuric and carbonic acids. Sulfur deposits itself sometimes from volcanic exhalations and this may have led to the conclusion that the universal acid was the origin of sulfur. But how fantastic the idea was that hydrochloric acid together with petroleum formed that sulfur! And still more fantastic was Hjärne's doctrine about the formation of sea water out of exhalations from the planets and the moon.

Yet Hjärne was one of the best propounders of the chemistry of his day. Many of the alchemist's writings are quite incomprehensible; some contain mystic recipes in which one can find scarcely any sense. The reason for the great lack of clarity lay in the spirit of the times which demanded of scholastic philosophies subtleties and hair splitting differences.

The concept of the three principles, nevertheless, was not shared by all the chemists of the period, as is demonstrated by the following roughshod criticism made by Hjärne's predecessor, Kunkel (1630–1702). He wrote in his "Laboratorium Chymicum" which was published after his death, "I, an old man, who for sixty years have occupied myself with chemistry, have never

yet chanced to discover the fixed sulfur nor how it enters into the composition of the metals. The philosophers differ among themselves about sulfur, so that one means thereby something quite different from another. Anyone has the freedom to christen his own child as he wishes. I hold this opinion: If you so wish, you may, without any opposition from me, *call* your donkey a cow, but you will never get anyone to *believe* that your donkey is a cow." Nevertheless, he, himself, believed that all metals contained quicksilver. Kunkel contested the explanation, current at that time, that the metals increase in weight when they are burned up, (oxidized), because they take up a weighable "fire-substance." It must be considered as rather strange that his co-worker, Hjärne, was not more strongly influenced by Kunkel's fairly sound views.

Chapter II

THE GROUND-WORK OF SCIENTIFIC CHEMISTRY

The fundamental principle upon which classic and medieval chemistry depended, and which hindered actual advance, was generalization without the use of observations based upon research. During the classical period a brilliant exception to this rule may be seen in the doctrines of the much-lauded Archimedes (287–212 B.C.) who first gave us ideas about equilibrium and hydrostatics in the field of mechanics. He discovered a method of determining the specific gravity of a body by weighing it in air and in water. In this manner he determined by actual experiment that a golden crown belonging to Hiero of Syracuse really was composed of gilded silver. By the use of his method it was possible to distinguish from each other the few metals which were then known. Throughout the middle ages this method, discovered by Archimedes, enjoyed great repute because of its practicality. Since the most important task of the chemist in that day was to be able to distinguish the different metals from each other the balance came to be called in Arabic writings the tool of the chemist.

Archimedes was in touch with the school of naturalists then in existence at Alexandria, a school which occupied itself with developing and chronicling the sciences, and from which come the principle treatises upon classical chemistry. From Alexandria chemical knowledge passed into the hands of the Arabs and thence to the Occidental lands.

Early in modern times there lived and worked in Italy a man of extraordinary genius and craftsmanship, Leonardo da Vinci, who, like Archimedes, was an engineer. Leonardo proposed the idea that the planets were made up for the most part of the same sort of material as the earth. This was in

opposition to Aristotle's belief that the planets were made up of finer material than the earth, an opinion which was even held by the great astronomer, Tycho Brache. Leonardo had quite a different view of combustion from that prevalent at his time. He said that air was used up in the burning process and that animals could not live in an air which could not support combustion.

The throne of Aristotle's infallibility began to totter. Aristotle's writings, which had ruled all concepts of natural science from the days of the beginning of our calendar until the dawn of modern times, at last came to be disputed to such a degree that Peter Ramus in 1536 nailed to the cathedral door in Paris a poster bearing the statement: "All Aristotle's teachings are false." This seemed to the prevailing Aristotelean school as black a crime as the negation of God. A short time later, Lord Bacon of Verulam (1561–1626) laid stress upon the fact that the only fruitful method of scientific research was based upon the results of experiment.

At that time people began to make careful researches on gases. The Dutchman, van Helmont (1577–1644) introduced the expression *gas*. Previously all gases had been considered as, and called, "air." Van Helmont proved however that the gas that we now call carbon dioxide, which results from the fermentation of beer or wine, or on treating chalk or potash with acids, and also issues from crevices in the earth, was of a very different nature from common air. Van Helmont also made diligent use of the balance and observed that no loss of material occurs in chemical processes; therefore he was a forerunner of Lavoisier in this discovery. Similarly he made the suggestion that it was a mistake to believe, as people claimed, that water could change into air or vice versa. Moreover he claimed that the metals could actually exist in their compounds despite the fact that these compounds had wholly different properties from the metals themselves.

The man who had more right than any one else to be called the father of scientific chemistry was Robert Boyle (1627–

1691). He took up the teachings of Democritus about atoms, which had already found a warm advocate in the French physicist, Gassendi (1592–1655). Boyle claimed that all atoms were made up of some sort of primal material, but despite the subtle interpretations made by the "peripatetics" (that is to say the followers of Aristotle), he permitted himself to doubt Aristotle's teachings about the four elements. Boyle progressed only from actual observations and he called "elements" that type of body which he could not further divide into other bodies. Naturally it was believable that man might succeed, long after, in breaking up even the material to which Boyle gave this definition of "element." Undoubtedly the elements were many more than four in number. The differences between a mechanical mixture of two substances and a chemical compound of them depended upon the fact that both substances retained their own properties in the mixture, while they lost them in the compound. Yet the two substances must both still exist in the compound for they could both again be obtained from it. Boyle carried out a remarkably great number of researches with the aid of the air pump, which had been invented by Guericke, and by the use of this instrument he discovered the law about the compressibility of gases which bears his name — Boyle's Law. By his experiments he discovered that ice contracts when it melts to water, a fact which contested that Platonic belief about the ancient elements. He found that the boiling points of liquids were lowered if the air pressure above them was lessened. He noticed that sea water was salt, not only on the surface as Aristotle had taught, but also even in the greatest attainable depths. Boyle was not able to free himself from all the mistakes of his day. Thus he thought that fire had weight because metals weigh more after burning (oxidizing) than before. Boyle's great contribution to the advance of science was that he abandoned the arbitrary, philosophical mode of thought and he concluded that "there is no other way to seek knowledge than by making varied research upon the things which are found in nature." He also

freed chemistry from its dependence upon medicine, so that it became a self-supporting science.

There lived in England at that time a very noteworthy man named John Mayow (1645–1679) by occupation a physician. He had made clear to himself that in air there was to be found a constituent which was also contained in saltpeter and which was used up in the process of burning the metals, i.e. oxidation or as it was then called, calcining; and that this constituent was also used up in the change whereby venous blood became arterial. After his early death his opinions, published in a memoir in the year 1674, fell more and more from scientific attention.

A man who contributed in a great degree to the overthrow of the queer doctrines of the alchemists was the Dutchman, Boerhave, of Leyden (1668–1738) the author of the best text-book in chemistry of his day, a book called "Elementa Chemiae" (1732) which was translated into many languages. He made a number of unsuccessful attempts to prepare other metals out of mercury. He found that heat had no weight by weighing a piece of metal in the cold and then again glowing hot. This experiment was of importance in throwing light upon the strange theory which was developed at that time in Germany by Becher and especially by Stahl (1660–1734). According to this theory combustion and the calcining of metals depended upon the passage from the burning body of a hypothetical substance called *phlogiston.* Yet at that time it was a well known fact that the metals in calcining took on weight. It is strange that this fact did not restrain Stahl from his odd notion. He himself said: "with calcining, the phlogiston departs, but it does not take any of the weight with it." Lemery next sought to clear up this peculiarity in the following way: When metals lost phlogiston they took up heat, which had a considerable weight. But that notion was disproved by Boerhave's experiment. Next chemists conceived of such venturesome explanations as that phlogiston had negative weight, (the Swede, Scheffer), or that phlogiston was lighter than air

and so lifted metals like an air balloon, thus apparently giving them a lowered weight, (the Frenchman, Guyton de Morveau). These notions however were opposed by Boyle's observation that the then known metals all had higher specific gravity than the corresponding metal oxides, (calcs).

The position was in itself untenable, yet the phlogiston theory was upheld for a century by such prominent investigators as Priestley, Scheele, Bergman, and Cavendish, four men who collected important material for further advancement of the science. Priestley, (1733–1804), was an especially successful experimenter, and he discovered a great number of gases, namely, nitrous oxide, nitric oxide, hydrogen chloride, hydrochloric acid gas, sulfur dioxide, silicon fluoride, ammonia, and most important of all, oxygen gas. In his investigations he made the important observation that green plants split up carbon dioxide in sunlight and give off oxygen, while the respiration processes of animals show an opposite action. Priestley also introduced the modern method of gas analysis with the use of the eudiometer.

At about the same time and independently of Priestley, Scheele in Sweden, discovered oxygen, nitric oxide, ammonia and also hydrogen cyanide, hydrogen chloride and chlorine. Furthermore he made an unusually great number of discoveries such as of manganese compounds, barium, hydrogen fluoride, molybdic, tungstic, boric and arsenic acids, in the field of inorganic chemistry, and also lactic, tannic, pryogallic, oxalix, citric, tartaric, malic, mucic and uric acids, glycerin and milk sugar, in the field of organic chemistry. As chemical discoverer of previously unknown substances the apothecary from Kõping, (a little Swedish town), stands without equal. Among other things he demonstrated that the residue, ("earth" according to Plato), which was found on evaporating distilled water after twelve days boiling in a glass vessel consisted of material dissolved out of the walls of the vessel. He lived from 1742 to 1786.

Cavendish (1731–1810) was notably distinguished as a physi-

cist, mathematician, astronomer and chemist. Among other things he measured the earth's specific gravity with great precision. He improved Priestley's eudiometric methods of gas analysis, and showed by these methods that air has practically the same composition everywhere. (Nitrogen was already known. Its nature as elemental material had been shown by Rutherford in Edinburgh in 1772). Cavendish's most important discovery was of hydrogen, and he demonstrated that water consists of hydrogen and oxygen, and therefore cannot be an element. He also proved the composition of nitric acid and the cause of water's "hardness."

Bergman (1735–1784) systematized the observations then at hand about the abilities of bodies to replace one another according to their positions in the so called affinity tables. He further rendered great service in analytical work. At first this latter had only been qualitative (if one omits the use of specific gravity determinations by Archimedes) i. e. people tried to determine the presence of certain substances but not their amounts. For qualitative analysis smell and taste were used to a great degree. One must often wonder how the chemists of that time for example Scheele, who worked with prussic acid, could come unharmed from researches thus made with the most poisonous substances. From early times came the use of coloring materials from the plant world to distinguish the presence of acids and bases. Gradually people found reagents which were specific for a given substance. Thus they passed over more and more to quantitative analysis. Even before the time of Boyle this had begun. Boyle developed analytical methods which were extended further by the work of the Dutchman, Homberg, the Prussian, Marggraf, and particularly by the Swede, Bergman, as well as by others. Bergman described a great number of compounds which could easily be analysed; adopted to analysis by weighing. It is plain that in doing this he foresaw that the compounds had a constant composition. Cavendish, of whom we have spoken above, gave a firm foundation to the analysis of gases.

A large number of new substances had thus become known through the work of chemical investigators, particularly Scheele. Among the new substances may be noted the elements, phosphorus (the German, Brand–1669), manganese (Gahn–1775), cobalt (the Swede, Brand–1773), nickel (Cronstedt–1751) and platinum (d'Ulloa–1738). The times were now ripe for a revolution of chemical theory, particularly through the discovery that the air contained oxygen and that this played the principal role in those processes that previously had been considered to be due to the disappearance of phlogiston. The man who first clearly realized this was Lavoisier (1743–1794) and on this account he is often called "father of modern chemistry." The first of November, 1772, he deposed with the French Academy a sealed communication. That body opened it the fifth of May, 1773. Within, it was stated that if a pound of sulfur was burned to sulfur dioxide then the latter weighed far more than a pound. One might make a similar observation in burning phosphorus to phosphoric anhydride. Lavoisier stated that the addition of weight depended on the taking up out of the air of one of its constituents. Lavoisier also stated that he believed the well known increase of weight of metals in calcining was due to a similar circumstance. Conversely, Lavoisier proved that in the reduction of metals out of their "calcs" an air was freed. He said, "I have carried out the reduction of litharge (lead oxide) in a closed vessel and I found that in the moment when the calc changes to the metal, a considerable amount of air is given off, a thousand times the litharge in volume." A little later, 1774, Priestley published his discoveries about oxygen and its ability to support combustion, so it became clear to Lavoisier that the air-constituent alluded to was oxygen[1] and he gave it the name "oxygen" (the acid former; previously it had been called "burnable air"). Later he made precise weighing experiments upon the oxidation and reduction of metals in a closed space and found that the total weight did

[1] Lavoisier visited Priestley and saw him make experiments upon oxygen gas, and cannot therefore be looked upon as the co-discoverer of oxygen.

not change. He concluded from this that nothing can be created out of nothing. "When one thing is made from another, in each such process there may be found just as much material before as after the process." These were almost the same words as had been used by Empedocles twenty-three centuries earlier. Lucretius, the Latin philosopher also says: "Nothing from nothing ever yet was born." But there is a world of difference between the philosophic hypothesis and the theory grounded upon research.

It should be noted that Lavoisier had numerous predecessors who came near to a correct conception about combustion. We have mentioned the genius, Leonardo da Vinci (1452–1519). This man, who accomplished marvellous work in all the arts and sciences of his time, also suggested a theoretical explanation of the problem of combustion. According to Leonardo air was consumed in the process of burning, and animals could not live in an air which, after bodies had been burned therein no longer could support combustion. Thus Leonardo discovered the fact that air consisted of two parts, of which one, now called oxygen, could support combustion and was necessary for the respiration of animals, while the other, now called nitrogen lacked these properties.

Most explicit of Lavoisier's predecessors in expressing his ideas was the English physician, Mayow (born in 1645) also mentioned above, whose untimely death in 1679 prevented him from elaborating his theory given out in 1674. He proved that saltpeter consisted of an alkali and an acid. Since saltpeter, like air, could support combustion and since alkali could not do this, Mayow claimed that the acid in saltpeter must have originated in part from the air. To this portion of the air, now known as oxygen, Mayow gave the name of "fire air." Antimony took on weight when it was calcined (or as now spoken of "oxidized"). It was difficult to understand that this could be due to any other cause than that it took up fire air out of the air. It was hard to fancy that, as was claimed at the time, the increase of weight could depend upon loss of

sulfur from the antimony. Fire air was necessary for the breathing of animals. In the process of respiration air lost volume. The blood going into the lungs was dark, but that leaving them was light red, for a chemical change had taken place by the action of fire air. If dark venous blood was allowed to stand in the air, its liquid surface took on a light red color by the action of the air, while the deeper layers remained dark. "The warmth of the blood," said Mayow, "I look upon as a result of the action of the particles of fire air upon the burnable constituents. If one sets certain minerals, for example marcasite in moist air they become warm in a short time because of the action of the particles of fire air. How much greater must be the warmth produced in blood since burnable substances occur therein in quantity and these become intimately mixed with the air (in the lungs)."

A very remarkable statement has been found by Klaproth in a Chinese manuscript of the eighth century. The author, Mao Khoa, reported therein that air was composed of two constituents, yin and yang. Yin could be removed from the air by the use of divers metals, or by sulfur, or carbon; — it must therefore have been oxygen. Yin could also be prepared from a certain mineral, the name of which is given. Klaproth presumes that this word meant saltpeter, but is not sure of this.

The Byzantines very probably knew of gunpowder in the seventh century, the Chinese surely in the tenth century. Saltpeter is a constituent of this. From China the use of gunpowder passed to Persia and Arabia, where saltpeter was called the Chinese salt, or Chinese snow. The Arabs probably taught the Europeans the art of handling gunpowder.

The great chemists at the end of the eighteenth century did not understand the simple truth in the teachings of Lavoisier, remarkable as this seems today. They had so habituated themselves to the old phlogistic theory, untenable to us, that they considered this theory more natural. Scheele, Priestley and Cavendish sought to defend the old teachings and it is

stated in Scheffer's preface of a new edition in 1796, of Bergman's "Chemical Lectures," that the new doctrines still were "very doubtful and open to contest." Priestley was a follower of the phlogiston theory until his death in 1804 at Northumberland, Pennsylvania, U. S. A., where he had come for religious freedom.

Torbern Bergman noticed that some metals could replace other metals from the water solution of a salt of the latter, yet the solution did not become either acid or alkaline, nor was a gas developed. To take an example which is made use of practically, if a copper salt such as blue copper vitriol (copper sulfate) is disolved in water and a piece of iron is laid in the solution, then the latter dissolves with the formation of iron vitriol (ferrous sulfate) and copper precipitates out on the piece of iron. Thus copper may be precipitated from solutions of copper salts by means of iron scrap. The commercial copper known as "cement" copper is made in this way. It is contaminated with iron and must be further refined if it is desired to obtain pure copper from it. Often poor grade copper ores containing sulfur compounds are worked in this way. Such ore is roasted with common salt. Copper salts form which are leached out with water, then iron scrap is added to this solution and the copper precipitates out. It is said that the iron precipitates an equivalent (literally: "of equal worth"), amount of copper. 63.4 grams of copper are precipitated by 56.0 grams of iron, so 634 grams of copper are said to be the equivalent of 560 grams of iron. Bergman, as an adherent of the phlogiston theory, claimed that the above amount of copper contained just as much phlogiston as did the above named amount of iron. But after Lavoisier had interpreted things otherwise, people said that the given amounts of copper and iron could each combine with one and the same amount of oxygen. Neither Bergman nor Lavoisier were quite correct in their ideas about this. It was J. B. Richter (1762–1807) who first cleared up the matter. He determined the amounts of different acids capable of neutralizing the same amount of alkali. In this determination he used

plant colors such as litmus to show by change of color when neutralization occurred. Thus he found the amounts of two acids which were equivalents of one another in neutralizing bases and also how great an amount of an acid was necessary for the neutralization of a given amount of a base. Richter named the study of these equivalent weights and their measurement, *stoichiometry.*

It was not however upon these observations that the new *atom* school arose but upon a knowledge of the composition of gases. The atom theory was proposed by John Dalton (1766–1844). Dalton at first was interested in meteorology and came to make researches upon the physical properties of gases as a result of this interest. Among other things he discovered that gases expand with rising temperature and all very nearly the same amount for the same increase of temperature. This law was rediscovered later and was studied more deeply by the Frenchman, Gay Lussac. If a gas is heated from 0° to 1°C at atmospheric pressure, with care taken that the pressure be unchanged, it increases its volume one two hundred and seventy-third. This number is not exact for all gases but is nearly so, and in general one can say that the deviation from it is smaller the more dilute the gas, that is to say the smaller its pressure.

The discovery however which lead Dalton to his great concept was that if two gases were made up of the same elements such as for example marsh gas and ethylene, where both are composed of carbon and hydrogen, then the amounts of hydrogen which in the two gases were bound to the same amount of carbon stood in a simple relation to one another, in this case as two is to one. In 8 grams of marsh gas there are 2 grams of hydrogen and 6 grams of carbon while in 7 grams of ethylene only one gram of hydrogen is bound to 6 grams of carbon. This behavior could be explained most easily if one assumed that both hydrocarbons (so called because they contain only carbon and hydrogen) were built up of particles of carbon and hydrogen such that each carbon particle weighed six times as much as each hydrogen particle. These particles were equiva-

lent to the atoms of Democritus. A particle of ethylene was assumed to be made up of an atom of carbon and an atom of hydrogen, while a particle of marsh gas was assumed to be made up of one atom of carbon and two of hydrogen. Dalton called the smallest particles of ethylene and marsh gas also by the name "atoms" whereas we nowadays call them molecules.

Naturally a single case of this sort of relationship was not sufficient to convince Dalton that his opinion was correct. A very similar case to that of the two hydrocarbons was to be found among the compounds of carbon with oxygen where in one compound, carbon monoxide, six grams of carbon held eight grams of oxygen, while in the other case, carbonic acid, (carbon dioxide), six grams of carbon held 16 grams of oxygen. Furthermore it was found that water vapor contained eight grams of oxygen to each gram of hydrogen. All these data could easily be reconciled one with another if one started out with the assumption that the hydrogen atom weighed one, and considered that the carbon atom had the weight six and the oxygen atom the weight eight.

From the composition of ammonia gas, which was found to be five parts of nitrogen to one of hydrogen, Dalton concluded that the weight of the nitrogen atom must be five. Dalton found an especially interesting state of affairs to hold for the compounds of nitrogen with oxygen. A molecule of nitrous oxide was found to contain two atoms of nitrogen and one of oxygen, while a molecule of nitric oxide was made up of one atom of nitrogen and one of oxygen. An "atom" of nitric anhydride he proved to consist of two atoms of nitrogen and three of oxygen. Dalton furthermore thought he had proven the nitric acid molecule to be made up of one atom of nitrogen and two of oxygen and that another nitrogen compound consisted of one atom of nitrogen and three of oxygen. These last two statements were not wholly true. They doubtless depended on some erroneous analyses. We know today that the oxygen compounds of nitrogen are such that two atoms of nitrogen hold 1, 2, 3, 4 or 5 atoms of oxygen.

This proposition of Dalton's is called the Law of Multiple Proportions. Dalton did not content himself with the determination of the relative weights of substances which entered into the composition of gaseous compounds, but he also investigated the composition of other substances such as sugar, ammonium nitrate, sulfuric acid, chalk, magnesia, soda, potash, compounds of iron and of other metals, and established in this manner their combining weights.

Dalton's determinations were not very exact and there is no doubt but that he justified them with the aid of his theory, a very grave fault, but he had the good fortune to make clear to his contemporaries that his combining weights, or as we say today, atomic weights, were of fundamental importance in the science of chemistry. A great number of practitioners of the science took upon themselves the task of accurately determining these atomic weights. Among these by far the foremost was the great Swedish scientist Berzelius (1779–1848), who set at the head of his splendid list of accomplished works the determination of atomic weights with the greatest possible accuracy. He thus created an epoch in chemical history, and was unsurpassed by those before him or for long after him as master of his science. By his work Dalton's theory was proven to be of fundamental importance.

A discovery about the laws of combination of gases which also became of fundamental importance in the development of chemistry was made by Gay Lussac in 1805. He showed that, if two gases enter into union with one another, then the volumes of the two gases which unite chemically, and also the volume of the resulting compound, stand to one another in a simple relation. Dalton had found such a regularity of action, but he did not understand its meaning and importance. Since the volumes of two gases depend upon their pressure and temperature one must always understand that the volumes of the different gases are all measured at the same temperature and pressure. If this condition is taken, three volumes of hydrogen combine with one volume of nitrogen to form two volumes of

ammonia. Two volumes of hydrogen combining with one volume of oxygen to form two volumes of water vapor, etc.

Gay Lussac did understand the meaning of his discovery and Berzelius made it still plainer. Berzelius assumed that equal volumes of two gases contained an equal number of atoms. Thus if two volumes of hydrogen combine with one volume of oxygen, then the resulting water molecule must be made up of two atoms of hydrogen and one of oxygen, and not, as Dalton, for the sake of simplicity, had claimed, of one atom of hydrogen and one of oxygen. Similarly the ammonia molecule must be made of one atom of nitrogen and three of hydrogen. Berzelius still called the smallest divisions of combined bodies, (such as water), atoms and not molecules. The change in nomenclature was made by Avogadro (1811) as we shall see below.

But another difficulty was encountered. It was found that if one volume of chlorine gas combined with one volume of hydrogen, then two volumes of hydrogen chloride were formed. According to Berzelius's theory this would mean that an atom of chlorine combined with an atom of hydrogen to make two "atoms" of hydrogen chloride. That is indeed impossible. From one atom of chlorine and one atom of hydrogen there cannot result more than one particle of hydrogen chloride. A simple way out of this difficulty was found in 1811 by the Italian chemist, Avogadro, who assumed that chlorine gas was made up of molecules and that these each consisted of two atoms of chlorine, and similarly hydrogen gas was made up of diatomic molecules. Then a molecule consisting of two atoms of chlorine can combine with a molecule consisting of two atoms of hydrogen to form two molecules of hydrogen chloride. Similarly one finds that *two* (volumes) molecules, i.e. *four* atoms of hydrogen combine with *one* (volume) molecule, i.e. *two* atoms of oxygen to form *two* (volumes) molecules of water. It is found that most of the gaseous elements, for example nitrogen, bromine and iodine, besides the above described, consist of molecules formed by the combination of two atoms. At higher temperatures the molecules of the two last-named elements decompose into single atoms.

Simple and attractive as was Avogadro's hypothesis, still it met with lively opposition and first began to be accepted in 1851 when Avogadro's countryman, Cannizzaro, adopted it and supported it by the mass of evidence then at hand in the field of organic chemistry. Since then Avogadro's hypothesis has been the most important single foundation-stone of chemical science, and it is always made use of in determining the molecular weight of gaseous substances. The difference of definition introduced by Avogadro between the term molecule and the term atom has been accepted without contest.

Long ago the alchemists made use of a sort of sign writing. Perhaps they did this mainly in order to give a mystic cast to their writings. The metals, of which at first only seven were known, were considered to represent the seven planets and were designated by the signs of the planets. Later when new metals were found new signs were used. The first among these, antimony, received the astrologic sign of the earth. Of early origin also were the signs for "element" and for the "principles." We represent below a few of the more important examples of the alchemistic signs:

gold (the Sun)

silver (the Moon)

quicksilver (Mercury)

lead (Saturn)

copper (Venus)

iron (Mars)

tin (Jupiter)

antimony (the Earth)

zinc

platinum

arsenic

nickel

bismuth

fire

water

salt

metal

saltpeter

silver-saltpeter (silver nitrate)

white arsenic (arsenious oxide)

These signs did not in any way indicate quantities of the substances, but only qualitatively the presence or use of a given substance. They give an interesting insight into the ideas held by the alchemists of the composition of various bodies. Thus the sign for water is the sign for fire turned upside down. These two "elements" were supposed to be the exact opposites of one another, for water is noted for its coldness and dampness, while warmth and dryness are properties of fire. Platinum had in its sign the combined signs of gold and silver, which indicated that they thought platinum was an alloy of gold and silver. The alchemists had signs not only for materials but also for all sorts of apparatus such as retort, receiver, crucible and also signs for the modes of procedure such as for subliming, distilling, calcining, precipitating, dissolving, etc., and for day, night, morning, hour, etc.

When Dalton produced his atomic theory he expounded it with the aid of new signs which indicated the amount which made up the atomic weight. Thus ⊙ meant one part by weight of hydrogen, (the same sign which the alchemists had used for gold); O was oxygen (8 parts by weight; Dalton wrongly took seven); ⊘ was carbon (6 parts by weight; Dalton took 5); a circle with a vertical diameter meant nitrogen (5 parts by weight); a circle with three rays was used for phosphorus (9 parts by weight); a smaller circle within a larger stood for chalk (23 parts by weight); etc. For some signs, those for the metals, he used letters, which thus made connecting links with the signs used by Berzelius. Thus Dalton indicated iron by I (38), Z (56), C, copper (56), L, lead (95), S, silver (100), P, platinum (100), G, gold (140). The figures given as combining weights are very interesting, for, when they are compared with the table which represents recent determinations, they show what great errors were to be found in Dalton's determinations of these numbers. Berzelius replaced Dalton's signs by the initial letters of the Latin names of the elements. Since the alphabet did not suffice to designate all the known elements for some he chose a characteristic letter-

combination from the Latin name. In recent years the values of the atomic weights have been the object of international agreements.

Most of the chemical elements are of rather rare occurrence in nature. F. W. Clarke in his book "Data of Geochemistry" has compiled a table of the elements which occur most abundantly in those parts of the earth which are available to us for examination, namely the atmosphere, the ocean, and the lithosphere, that is to say the solid earth crust to the depth of ten miles. The masses of these three portions of the earth make up 0.03, 6.97, and 93 percent respectively of their total mass. The chemical elements occur in these comparatively well studied portions of the earth in the following percentages:

Oxygen	50.02%	Chlorine	0.20
Silicon	25.80	Carbon	0.18
Aluminium	7.30	Phosphorus	0.11
Iron	4.18	Sulfur	0.11
Calcium	3.22	Fluorine	0.10
Sodium	2.36	Barium	0.08
Potassium	2.28	Manganese	0.08
Magnesium	2.08	Nitrogen	0.03
Hydrogen	0.95	Strontium	0.02
Titanium	0.43	The other elements	0.47

The dominating importance of oxygen, and next of silicon is apparent. In combination these two elements form silica which is a component of all silicates. These form the principal mass of the lithosphere, 59.8% of which is composed of silica. Aluminium is also found in great quantity in the silicates of the earth-crust, and so has a high place in the table. The same is true of the metals next following. Of these iron would undoubtedly take a higher position if a calculation could be made for the whole earth. Since the mean density of the earth is 5.4, about double the mean density of the lithosphere, it is possible that the principal constituents of the interior mass are bodies of specific gravity between 7 and 8. These figures agree with the specific gravity of some of the commonest metals. Iron is commonest of all and has the

specific gravity of 7.9. It is possible therefore, as Chladni claimed long ago, basing his hypothesis on the phenomenon of earth magnetism, that "iron must occur in great amount in the interior of the earth." This is also likely because of the extremely great part played by iron everywhere in nature, for example in meteorites and in the sun (to judge by the solar spectrum). The high figure for hydrogen depends upon the fact that it makes up about 11% of the content of the oceans of the world. The lithosphere contains only about 0.22% of this element. Similarly it may be said about nitrogen, great as is its importance, that it could not be included in the above table but for the fact that it is the principal constituent of the atmosphere. The smaller proportion of carbon is noteworthy. It occurs principally in the form of carbonates, for the most part as limestone. Phosphorus and sulfur which are thought of as important elements in both the inorganic and the organic worlds are found in only 0.11% or slightly more abundant than fluorine. As heavy a body as copper, which we ordinarily consider a very common material does not appear at all in the table (its figure is 0.01%, nickel 0.02%).

Because of the ability of oxygen to enter into combination with the most varied elements it is natural to take its atomic weight as a basis for the determination of the atomic weights of the other elements. For very different reasons from Dalton one may take the atomic weight of the lightest of all elements, hydrogen, as unity. Oxygen's weight then becomes 16. Later, more accurate determinations have shown that if oxygen is taken at exactly 16, then the atomic weight of hydrogen is really 1.008. Because of their great importance to chemical science and their practical use, atomic weight determinations have been carried out with especial care in the last decade. Foremost among those in recent years who have done especially meritorius work in this field are the American, T. W. Richards and the Swiss, Phillipe A. Guye.

The chemical symbols are of great assistance to the chemist for describing the results of chemical experiments by the use of

chemical formulæ and equations, which indicate at one and the same time the nature of the reacting bodies and their proportions by weight. If, for example we wish to prepare hydrogen chloride, (hydrochloric acid), it can be done by adding sulfuric acid to common salt, (NaCl), and then distilling off the vapor that is formed, which can be taken up in water. The process may be represented quite simply by the formula:

$$\underset{\text{(sod. chlor.)}}{2NaCl} + \underset{\text{(sulf. acid)}}{H_2SO_4} = \underset{\text{(sod. sulf.)}}{Na_2SO_4} + \underset{\text{(hydrogen chloride)}}{2HCl}$$

$2NaCl$ is $2 \times (23 + 35.46) = 116.92$ gms. salt. H_2SO_4 is $(2 \times 1.01) + 32.06 + (4 \times 16) = 98.08$ gms. sulfuric acid. Out of these is formed $(2 \times 23) + 32.06 + (4 \times 16) = 142.06$ gms. $Na_2 SO_4$ and $2 \times (1.01 + 35.46) = 72.94$ gms. hydrogen chloride (a gas which when dissolved in water is called hydrochloric acid).

In the chemical formulas we write on the left side of the equal sign the materials that enter into the reaction, in other words the things used in the process. On the right hand side of the equal sign we write the products we get from the reaction. In the process given above we can make the reaction go to completion by driving off the last traces of the hydrogen chloride which may be done by warming the vessel. If water is present in good quantity and we do *not* heat the mixture, then the newly formed products dissolve in the water, just as do the substances started with and we get a mixture which contains all four of the substances named in the equation. Under this condition it has been found that the process proceeds only about one-third toward completion. We say that a *chemical equilibrium* has been reached between the four bodies. If we wish to indicate in the equation that equilibrium has been reached we can substitute for the equal sign two arrows pointing in opposite directions, one over the other: $\rightleftarrows$ as van't Hoff suggested. In place of the equal sign of Berzelius a single arrow is also sometimes used, which by its direction indicates the direction of progress of the reaction. This latter mode of

representation is particularly used when one wishes to show that a process goes to completed reaction in a given direction.

In the example which has been given above, by heating the mixture we can drive out all the hydrogen chloride (and water) and thus make the reaction proceed to completion. Naturally one can break off the distillation whenever one wishes and thus can drive the process to whatever stage is desired. That this can be done depends on the fact that one of the products, here the hydrogen chloride, can be removed completely. Naturally it is also possible to make the reaction as incomplete as we wish by adding only small amounts of sulfuric acid to the salt. We can also make the process go almost as near to completion as we wish by adding an excess of sulfuric acid to the salt. If in a reaction one of the newly formed products separates as a *solid* as a result of its insolubility in the reaction mixture then the process can likewise go practically to completion. The completion of a reaction generally depends on the formation of a gas or a solid. This is because these products separate from the reacting mass and thus are not further acted upon by the other bodies present. It was the greatest scientific contribution of Berthollet (1748–1822) that he recognized the importance of this fact in determining the course of a reaction.

Chapter III

FIRE, OXIDATION AND REDUCTION

The conditions which have raised man to a real cultural life have been dependent upon his ability to make use of the powers of nature. The use of fire, above all else has been of extraordinary importance. Its value to man found early expression in the myth of Prometheus who stole fire from the gods and thereby became protector of mankind. Even the sagas of the northern peoples contain a rather similar account illustrating the great importance of fire. These sagas relate how the fire-god Heimdall, a being of marvellous beauty who was born of the sparks from the millstone of the giants, came to mankind in the guise of a fair-haired youth to present the blessings of civilization.

Fig. 1. Drilling Fire

It is claimed that various native tribes in the New Guinea and in West Africa have lacked knowledge until quite recent times of how to prepare a fire other than by lighting one from fire already existing. It is possible that the original fire was caused by lightning. But it is much the commoner case that even savages of low development understand how to prepare fires. Throughout a great variety of different tribes and races fire is produced by rubbing two sticks of wood together, commonly so that a cylindrical trepan is rapidly revolved in a hollow in another stick. Around the hollow is laid easily combustible material such as dry leaves or twigs, which catch fire when the

temperature in the bore-hole rises sufficiently. The American Indians "bored" fire in much the same way, using a spindle-whorl driven by a bowstring. Figs. 1 and 2.

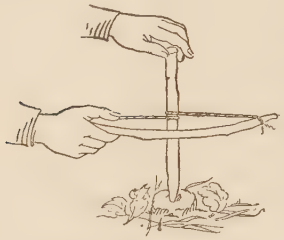


Fig. 2. Bowing Fire

Instead of turning or boring fire one can also "saw" fire by drawing a wooden stick back and forth over another stick lying crosswise to the first. See Fig. 3. The rubbing stick is moved in rapid time and with strong pressure across the other until it begins to smoke and finally a spark appears which is quickly caught by an assistant upon punk-wood. Various woods might be used for the rubbing. Such a simple rubbing method should be of use to anyone in forest or field who might lack other source of fire. Another method is to take a small rod or twig, best of alder, and pressing it between a pair of dry sticks, rub until it takes fire. Fire obtained in this way is called "rub-fire." This method's great age may be hazarded from its simplicity and also from its usage for religious purposes such as for the lighting of the Yule-fire or of fires upon certain church feast-days, as well as from its traditional use in sorcery, such as in charms against witchcraft. Farm creatures were made to inhale smoke from such a fire to protect them from falling into the water or from becoming sick or coming to any other harm.

Fig. 3. Rubbing Fire

Another fire-lighter still in use among civilized folk is the "fire-striker." At some early date it must have been discovered that sparks could be formed by striking two stones against one another. These sparks could be used to light some easily burnable substances. Different sorts of stones do not produce this effect equally well however, and it was soon found that a flint or some other par-

ticularly hard stone when struck against pyrite was of particular use for the purpose. Pyrite is a mineral consisting of sulfur and iron, of chemical formula, FeS_2. (The English word "pyrite" comes from the Greek word for "fire" and we have the same root in our word "pyre" — Tr.) The Eskimos use this combination for obtaining fire, sometimes striking two pieces of pyrite against one another. It is claimed that the discovery of pieces of pyrite about dwelling places in Belgium that were inhabited at a long-distant time (about 25,000 years ago), when reindeer were common in those regions, is an indication that those ancient people knew how to kindle fire with pyrite. The people of the Stone Age and of the Bronze Age certainly knew this art. At a dwelling place in Gullrum, Sweden, which was inhabited during the Stone Age, pyrite has been found; and in barrows and at many prehistoric dwelling places this mineral is to be found. In place of pyrite came the use, after their discovery, of iron and steel, and flint and steel have been used over the whole civilized world until very recent times. The use of flint and pyrite was continued in the ancient world till shortly before the beginning of our calendar. From their usage both the flint and the pyrite have borne the name of "fire-stone." (Thus German "Feuerstein," English "Pyrite," etc.) Fig. 4 represents the use of the fire-steel and flint.

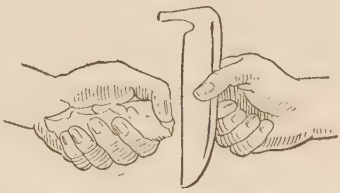


Fig. 4. Flinting Fire

From the pyrite or the iron by the action of the harder flint a little flake is struck off, and this flake is made glowing hot from the heat which the blow produced. Iron or steel is of great usefulness for this purpose because the glowing flake of metal is burned by the oxygen of the air. The development of heat which this latter process brings about is far greater than that arising from the blow itself. The action of pyrite is somewhat similar. When this is heated it gives off half of its sulfur,

which burns, and the remaining iron sulfide burns also in the oxygen of the air to iron sulfate ($FeSO_4$). The brightly glowing particles so obtained can be caught in some easily combustible substance — commonly called "tinder." Charred linen is often used for this purpose, or cloth dipped in niter solution and then dried, or in former times most commonly punk-wood. By the aid of the flaming tinder one can light larger bodies of fuel.

All these methods, especially the "fire-rubbing" can be accomplished only with considerable labor. So to avoid the necessity of preparing fire too often, people in former times kept the fire burning through the whole twenty-four hours. Knowledge of the immense importance of fire to man, and of the antiquity of its use gave it a religious stamp, so that each temple hallowed an "undying" fire; for example the Persians, and also the Romans who consecrated the vestal virgins to tend the holy fire. In the Catholic lands one often sees burning candles or lamps before holy pictures.

That steel and flint were believed to be endowed with supernatural properties may perhaps be remembered by older people from the superstitions of their childhood. According to Keyland, in Sweden, "No one dared to go over a water-course without carrying a fire steel on his person for otherwise he might be overtaken by some sickness. If milk was to be delivered to a neighbor, sparks should be flinted over it, and similarly over water brought indoors after sundown. Sparks should be struck with a steel over fishlines. Disease could be driven away by laying a fire." It has been noted that among the Laps the adults increase the marriageability of their children by flinting fire over them. Finally there is the old saying that, "Fire and steel are cure for all."

The old fire striker has a modern counterpart in the cigar-lighters which have come into vogue in those lands where state monopolies have made the cost of matches artificially high. This lighter consists of a piece of iron which contains a little of the rare metal cerium. If, after opening the cover of the box,

one strikes or rubs the stick of cerium-iron alloy against a side of the box which is covered with a plate of roughened metal, sparks appear which fall on a wick contained in the lighter. This wick is either moistened with some easily combustible oil or is impregnated with niter. The cerium lighter is also used to light gas-ranges and the wicks of petroleum lamps, etc.

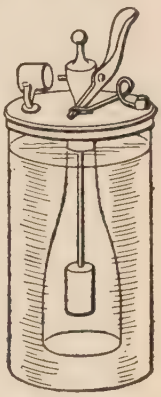


Fig. 5. Döbereiner's Fire-lighter

After the discovery of hydrogen gas, which is very inflammable, it was sought to make use of this for the construction of a fire-lighter. The hydrogen gas can be prepared by the action of zinc or iron upon an acid, for example on dilute sulfuric acid. The hydrogen can be gathered in a bell-shaped glass vessel, which vessel is drawn out above into a tube closed with a stop-cock. The hydrogen gas steams from the tip of this tube when the stop-cock is opened and can be lighted by means of an electric spark. This invention, which was made in 1770 by Fürstenburg of Basel, was improved in 1824 by Döbereiner who let the hydrogen gas stream out onto a piece of very porous platinum — the so-called platinum sponge. Large amounts of hydrogen gas condense upon this material and this causes a development of heat sufficient to set fire to the hydrogen. (See figure 5, Döbereiner's fire-lighter.)

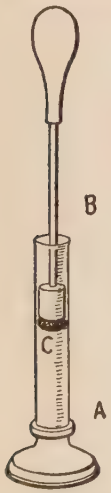


Fig. 6. The Pneumatic Tinder Box

Of a little greater antiquity than the above was the pneumatic lighter (Fig. 6) which consisted of a glass cylinder of narrow bore AB with a piston B, which fitted the cylinder and was oiled at the surface of contact. On driving the piston rapidly inward with a powerful push on its handle the air in the cylinder was rapidly compressed, and a sufficiently great development of heat occurred so that a

bit of tinder c, caught fire and this fire was transferred to a sulfur-tipped stick, with which dry wood was then lighted. This pneumatic lighter, still used today to demonstrate the "gas laws" to physics classes, was in actual practical use up to the beginning of the nineteenth century.

Yet all these fire lighters were not very convenient, and they were replaced by the so-called *chemical lighter* (Fig. 7) the first type of which was invented by the Frenchman Chancel in 1805. It was based on the fact that if potassium chlorate is treated with sulfuric acid, chlorous acid is formed and this is a very powerful oxidation agent, i.e., it is a body able to oxidize or to saturate with oxygen, (cause to combine with oxygen), such burnable bodies as powdered carbon, sulfur, sugar, etc., so that they catch fire. To make use of this property for lighting a fire, wooden sticks were employed one end of which were coated with a thin layer of sulfur. At the tip of this sulfured portion there was fastened an ignitor which consisted of a mass of potassium chlorate and sugar, both in powder form, with a gum as binding material. When the ignitor was dry the match was ready. In using it the ignitor-end was dipped into a little bottle which contained asbestos wet with concentrated sulfuric acid. At contact between the ignitor and the acid the sugar in the tip was first lighted, next the sulfur and finally the wood of the match stick. Such matches were long held in high esteem.

Fig. 7.
The Chemical Lighter
Ancestor of the Match

Another kind of match was the *Congreve's striker-stick*, invented by Trevany in Vienna in 1832. Here the ignitor, which was fastened to the tip of a stick which has been given a sulfur dip, consisted of a mixture of potassium chlorate and antimony sulfide (antimony glance), with gum. It was lighted by drawing the tip rapidly over a piece of sand-paper which was held

folded between the fingers. This type of match had the drawback that the tip was often lost-off in striking the match. Hence it has today been replaced by the types of striking matches using phosphorus.

Phosphorus was discovered in 1669 by a merchant named Brand, of Hamburg, Germany, who to better his failing business, dabbled in alchemy and particularly in attempts at gold-making. In his researches he once prepared a peculiar light-yellow, cloudy, dirty, semi-transparent substance, which had an onion-like odor and which shone in the dark, whence it was given the name of phosphorus, (light-bearer). It caught fire very easily and burned with development of a heavy white smoke (of phosphoric anhydride). The discovery awakened unprecedented attention and the new substance came to be considered as worth its weight in gold.

Gradually other chemists uncovered the method of preparation which had been held secret by Brand. Among these investigators were Kunkel (1676), and Boyle (1681) who made a fortune from this process. Gradually people found phosphorus in various tissues and materials of the animal body,— Brand had first prepared it from urine, and in 1769 Gahn discovered its presence in the bones of animals. Sheele in 1775 set down a method which is still quite widely in use for the preparation of phosphorus from the ash of burned bone. This ash consists in part of calcium phosphate. It was to be treated with sulfuric acid when an acid-calcium phosphate was formed, and this latter was ignited with carbon; the phosphorus distilled off in gas form and was condensed to a solid by leading it into water.

Phosphorus was soon made use of as an ignitor substance. It was not at first understood how to prepare it unmixed with impurities. The first phosphorus matches were manufactured in 1816 by the Frenchman, Derosne. This industry was taken up on a large scale in 1832 by Kammerer in Ludwigsburg and also at about the same time by an English apothecary, John Walker. Match tips were made of potassium chlorate mixed

with phosphorus, but these lighted with explosive throwing-off of small burning drops. Böttger in 1834 substituted a mixture of potassium chlorate and lead nitrate. Better and better recipes for the preparation of matches were gradually evolved, for example by the famous chemist, Wöhler (1854) among others.

The phosphorus sticks were in many respects admirable, and the match industry was greatly advanced by their introduction. But they also possessed some very inconvenient qualities. Because of their easy combustibility they caused accidental fires. The great toxicity of the phosphorus gave rise to many poisonings both unintentional and deliberate, and the workmen in the match-factories were attacked by a dangerous disease of the jaw-bone and the gums, the phosphorus necrosis.

But meanwhile Schrotten had discovered in 1847 that if the yellow form of phosphorus was heated to 260° in a closed vessel it passed over into another form, the so-called red or amorphous phosphorus and this had quite different properties from the yellow phosphorus. It had, as its name implies, a dark red color, did not shine in the dark, did not catch fire at low temperatures, and above all was of value because of its non-poisonous qualities. The match industry accepted the new discovery with enthusiasm. Attempts were begun to replace the yellow by the red phosphorus. But after a long series of researches it was found impossible because the red phosphorus did not catch fire easily enough. However it was only necessary to wait a while, till in 1848 Böttger in Frankfort hit on the happy idea of putting the red phosphorus on the surface upon which the match was to be struck. He mixed the red phosphorus with manganese dioxide while his match tips were made up of a mixture of potassium chlorate, antimony sulfide and gum as a binding material. Thus was discovered the safety-match. Today the old style phosphorus match has been forbidden in many lands and has been replaced by the safety match. Since however many people considered it desirable to be able to scratch the match on any desired surface,

if not too smooth, phosphorus matches have been invented in which the phosphorus itself is replaced by phosphorus sulfide ($P_2 S_5$) which is comparatively harmless. In addition to this latter substance the match tip contains potassium chlorate and sometimes glass-powder. Such matches were proposed by Sevene and Cahen in the year 1897 and have been extensively used in some countries, for example in Belgium.

The manufacture of safety-matches has been an extremely important industry in Sweden. It can be considered as an example of the growth of a great industry by force of enterprise and inventive genius in spite of the fact that the raw materials had to be brought from other lands. The body of the match, aspen-wood, comes mostly from Russia. Formerly also the potassium chlorate used in the match-tips was imported, but now it is manufactured in the country.

Safety matches have gradually been bettered. That they may burn better they are impregnated with paraffin after the sticks have been dried thoroughly by rubbing them on an almost red-hot plate. The tips are generally made of potassium chlorate, with lesser amounts of antimony sulfide, potassium bichromate, iron oxide and manganese dioxide, with gum as a binder. Occasionally also red lead, carbon, or sulfur may be used. The striking surface on the box is coated with a mixture of red phosphorus and antimony sulfide sometimes mixed with finely powdered glass or with iron sulfide to increase the friction. There is some inconvenience in the fact that occasionally the end of the burning stick may fall off and set fire to paper or clothing. To prevent this the wood of the stick is impregnated first with a solution of a salt like alum or aluminum sulfate, sodium phosphate or ammonium phosphate. The wood is thus made less combustible, it is the paraffin which burns and the carbonized wood is strengthened by the salts it contains so that it does not break off after the tip is burned.

Van Helmont said that fire was a gas or smoke which glowed. The latter idea is more nearly correct. Gases give forth only a faint light in burning as can be seen when charcoal burns.

Carbon is first oxidized to carbon monoxide (CO) consisting of 12 parts of carbon and 16 of oxygen. This gas then burns with a very faintly luminous blue flame to carbon dioxide, (CO_2, carbonic acid), which contains 32 parts of oxygen to each twelve of carbon. Similarly the sulfur vapor which forms when sulfur is lighted burns with a very faint blue flame to form sulfur dioxide (SO_2), which has a characteristic choking odor. The vapor of alcohol also burns with a very faint blue flame to form carbonic acid and water and even ordinary illuminating gas burns in a similar way when sufficient air is supplied, as for example in a Bunsen burner or in cook stoves, displaying only a faint green flame. The fact that a candle flame or gas flame shines with a powerful white light is because the vaporized oils of the tallow or the illuminating gas partly decompose on heating with the formation of fine particles of carbon (soot) and these latter glow brightly when they themselves are burned in the outer part of the flame. The heat results from the chemical reaction, which is called oxidation, i.e. the adding of oxygen to the burning substance. At low temperatures this reaction goes so slowly that appreciable increase of temperature may not occur, so the burnable body is not heated to glowing. Ignition with production of flame or embers takes place only if the temperature gets high enough so that the process of oxidation goes on with sufficient speed for the temperature to more than maintain itself and to increase, that is to say when the developed heat cannot pass away or radiate just as rapidly as it is produced by oxidation. The temperature that is necessary for the burning of a combustible substance with the appearance of flame is called the firing point of the body in question. This point for most ordinary fuel materials lies quite high. But various organic liquids such as zinc ethyl are known, which catch fire when they come in contact with the air. A gas that lights at room-temperature or even lower if it comes into contact with the air is hydrogen phosphide (phosphine) which is formed when phosphorus is heated with an alkali such, for instance, as lye, or caustic soda or lime slaked in water. Bub-

bled from a water surface, gas rings form which catch fire. The gases after burning are warm so they rise carrying the product of the burning, phosphorus anhydride, in the form of white smoke-rings. The hydrogen phosphide has the formula PH_3 or 31 parts of phosphorus and three parts of hydrogen. There is always formed with it a tiny bit of another phosphorus hydride, PH_2, containing only two-thirds as much hydrogen as did the first named compound. This latter compound causes the self-lighting of the mixture on contact with the air. Fig. 8.

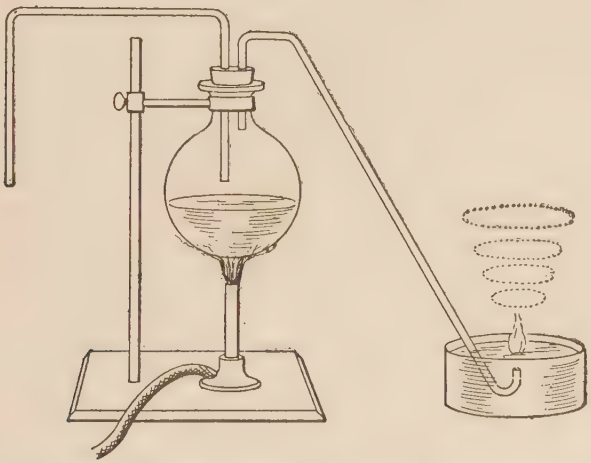


Fig. 8. Blowing Smoke Rings with Phosphine

Phosphorus itself has a very low firing-point, namely about 50° (122° F.) and occasionally as low as 40° (104° F.)[1] When in finely divided condition, for example when it has been crystallized from a solution in carbon di-sulfide which has been poured out onto filter-paper, it can catch fire by itself at room temperature. Because of the easy combustibility of phosphorus it is stored under water. In the air it oxidizes in such a way that ozone (O_3, a sort of condensed oxygen which normally is O_2) is formed. The lowest temperature at which

[1] Temperatures not otherwise designated are in Centigrade degrees.

hydrogen gas catches fire in oxygen is about 830° (1526° F.), although Helier claims that a slow combustion has set in at 200° (392° F.). We have already seen that when it is made to stream out against a platinum sponge it will light at ordinary temperature. It condenses very greatly in the porous platinum sponge and this action brings about the start of the combustion. The platinum sponge is said in this case to exert a catalytic action. Even the presence of a small amount of moisture will accelerate the burning. Platinum exercises a similar activity in many other cases, for example in bringing about the oxidation of alcohol to acetic acid. All finely divided or porous solids exert a catalytic action but different ones are of quite different activity. As one example may be cited the fact that cotton waste moistened with oils often causes accidental fires by setting itself afire (spontaneous combustion). Catalytic oxidation has been put to a most practical use in the so-called process of surface combustion. This latter has come to be used to a considerable extent both in industry and in the household, particularly in England and America. The first observation in this field was made by Davy in 1817. He introduced a slightly warmed platinum filament into a mixture of illuminating gas and air, taking care that there should not be so much air as to form an explosive mixture. The filament was warmed by a burning without flame of the illuminating gas on its surface to such an extent that it came to glowing red heat. This glowing did not cease until nearly all the oxygen was used up. This phenomenon was later investigated by various noted scientists of the first half of the last century, such as Thomas Graham, Dulong and Thenard, and also by Faraday (1834) who gave the correct explanation. The gas which was burned by the oxygen was taken up in the surface layer of the solid body (the platinum) and in this surface the chemical reaction went on. The platinum metals seem to be especially useful for this surface-combustion without flame and at low temperatures. The Dobereiner fire-lighter described above resulted from these early investigations.

The man who was foremost in introducing surface combustion into industrial use was Prof. W. A. Bone whose first investigation goes back to 1887. He then studied the burning of carbon monoxide and of hydrogen at the surface of various metals, oxides, porcelain and fire-clays. All solid bodies seemed to serve this same purpose but to different degrees. But he found that this difference of power lessened with higher temperature and nearly disappeared at a strong glowing-heat.

Fig. 9 shows a plate of porous material which is fastened in a

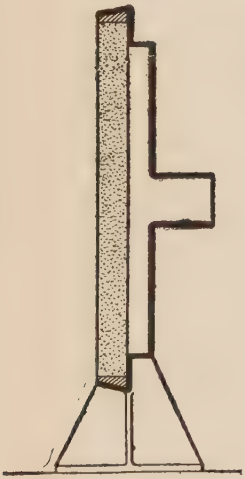


FIG. 9. SURFACE COMBUSTION PLATE

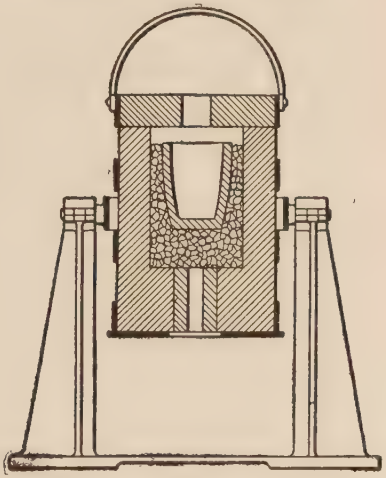


FIG. 10. SURFACE COMBUSTION CRUCIBLE FURNACE

tight metal casing into which common illuminating gas is led through the tube on the right-hand side. The gas goes through the porous plate and is lighted on its further, outer side (to the left in the figure). Air is now supplied to the gas stream, bringing sufficient oxygen to burn the illuminating gas. The flame then disappears from the surface of the plate, which shines forth with a strong glowing. The metal casing remains quite cold. The glowing area extends only to a depth of 1 to 3 millimeters below the surface of the plate. Cooking vessels can

be placed directly over such a plate. It has been found by trial that nearly double the effective heat is obtained in this way as compared to ordinary cooking over gas. Fig. 10 shows a crucible set in a jacket of granular fire-resistant material through which streams from below a mixture of illumi-

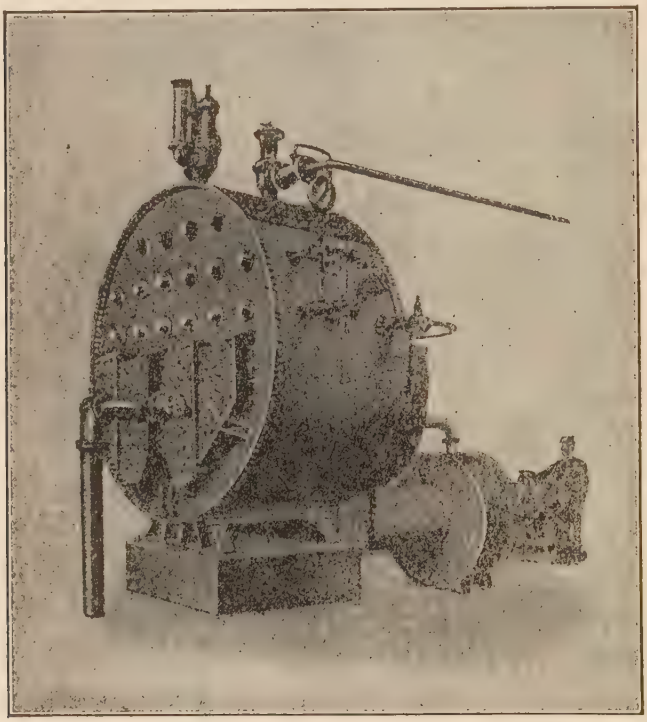


FIG. 11. STEAM BOILER FIRED BY SURFACE COMBUSTION

nating gas and air. The burning gases go out through an opening in the cover over the crucible. This method has also been used for firing boilers, (Fig. 11) the tubes of which are filled with fire-resistant material. Ninety percent of the heat of combustion is utilized while the best sort of boiler heated with coal utilizes only about 75%. This is because no unburned

gases are lost up the chimney and, besides, the combustion gases leave the boiler at a very low temperature 95° (203° F.) in the machine based on surface combustion. The major part of the heat is given over to the water in the front section of the tubes where the temperature amounts to 1400° (2552° F.) (about 30 cm. back from the front ends of the tubes, where the gas-mixture enters). The actual front ends of the tubes are comparatively quite cool, (i.e. at the temperature of the water within.) This constitutes a great advantage. At the other end of the boiler the gases pass out of the tubes at about 200° (392° F.). They finally pass to the chimney at 100° (212° F.) being led over a pre-heater from which the boiler is fed with water. The tubes are very short, only one, to one and three-tenths meters in length, so the boiler takes up much less room than a common boiler, which is also one of the advantages of this new type. This means of course that the steam formation per sq. meter of surface is in the same degree greater, (about 3.3 times that of the common boiler). One might suppose that the tubes would suffer a greater degree of strain as a result of the high working temperature, but they are found not to be harmed in the least. This possibly has some connection with the fact that no boiler scale is deposited in the tubes. Very likely the boiler-scale does precipitate, but it is blown out automatically when it reaches a thickness of about 0.3 cm. To all appearances combustion technique has received a very important advance in the introduction of surface combustion.

A similar surface combustion takes place in the burning of anthracite coal, which contains iron sulfide — not the common iron sulfide, pyrite, which crystallizes in cubes that belong to the regular crystal system, but the so-called *marcasite* which crystallizes in the rhombic system. Marcasite weathers rapidly in the air, and in this process it is oxidized. So great a development of heat can occur in this process that self-lighting of the coal may result.

An oxidation process which plays the greatest of roles in

living nature is that of breathing. Priestley made the discovery at an early date that the animals in breathing take in oxygen gas and breath out carbon-dioxide. At the same time they also give off water-vapor. The breathing can be considered as a slow-proceeding combustion by which the organic bodies found in the blood and containing carbon and hydrogen are oxidized by the oxygen taken in in the breathing to form the carbonic acid and the water which is expired. The warmth produced by the process is of use to the animal body. This type of breathing is to be found also among the plants when they are in the dark. But green plants which are illuminated by light behave entirely otherwise, as Priestley noted. They take carbonic acid out of the air and change this in the presence of water into carbohydrates and then give off oxygen.

If one cuts off portions of plants and places them in a heap, the life-phenomena and the respiration go on for some time, as long as the water content does not become less than a certain amount — about 40% of normal. A development of heat results which cannot be radiated away as fast as it is produced, so the temperature may rise until the material chars, and when this occurs the plants may even catch fire. It has been observed that certain micro-organisms contribute greatly to this development of heat.

That carbonic acid is formed during the combustion of our ordinary fuel materials such as illuminating gas, or that it forms during respiration, can easily be observed by leading the combustion or respiration gases through a tube into a flask which contains a solution of slaked lime — so-called, lime water — or into a solution of baryta in water. The lime water contains calcium hydroxide and the baryta water contains barium hydroxide, which have the property of forming with carbon dioxide a precipitate of calcium or barium carbonate, respectively, while the water which was bound up in the hydroxide is freed. The calcium and barium hydroxides are said to serve as reagents for carbonic acid, for even a tiny amount of the carbon dioxide gives the characteristic white precipitate when

it comes into contact with a water solution of either of these two hydrates. That water vapor is also given off in breathing may readily be seen by breathing on a cold glass surface, for example a window-pane

The heat which is freed in the process of respiration is used to hold the body at a higher temperature than its surroundings, and also to evaporate water from the body-surface. By regulation of the amount of food-substances which become fuel-material and of the evaporation which lowers the temperature when this threatens to become too high, the body temperature of the warm blooded animals is held almost unvarying.

In nature many slow processes of oxidation occur. The most important of these is the slow decaying process of dead organisms, which is brought about by the action of bacteria. It had been calculated that the plants take up about a 37th part of the carbon dioxide of the air each year. If no carbon dioxide were returned to the air by the combustion or decay of plants, the carbonic acid content of the air would be exhausted in as short a time as thirty-seven years. Burning of fossil fuel, especially of hard and soft coal, peat and petroleum, supplies only about one-eleventh as much carbonic acid. So this does not begin to replace the amounts of carbonic acid taken out of the air by plants. There is to be found no inconsiderable amount of carbon dioxide dissolved in the water of the ocean, and it is very likely that should the carbon dioxide content of the air become lowered, part of this would be given back to the air. But even with this reserve the carbon dioxide supply would not serve the needs of the plants for longer than a few hundred years. The decay or burning of dead plants is therefore of extreme importance for the maintenance of the equilibrium of nature.

Another slow oxidation process occurs in weathering. We have seen above how the weathering of marcasite can develop great heat sufficient to set fire to an anthracite coal containing it. Commonly however its weathering process goes so slowly that no appreciable temperature increase occurs. A similar

case is the oxidation of iron compounds. This reaction can occur in two different degrees of oxygen saturation. We have seen a similar example in the case of carbon which has two different degrees of oxygen saturation, a lower, carbon monoxide, CO, and a higher, carbon dioxide, CO_2. For the change of the former to the latter more oxygen is needed. Similarly when iron salts of the lower degree of oxidation — the so-called ferrous salts — are oxidized up to salts of the higher degree of saturation, called ferric salts, oxygen is required. This oxidation process takes place so slowly, however, that no fire-phenomena are brought about.

In the same way even metallic iron is oxidized in the presence of oxygen and water. The substance which is formed is iron rust. It consists of a compound of iron oxide and water called iron-oxyhydrate. By heating it strongly one can drive off the water and get pure iron oxide. Iron objects which are to be exposed to the action of moist air, if they are not to rust, must be coated with some protective coating. This often consists of varnish or paint; in other cases a protective metal such as tin or more commonly zinc is used. Iron coated with zinc is called galvanized iron. The rusting of iron takes place so slowly that fire does not result.

The opposite process to oxidation is called reduction. If for example one takes away from iron oxide its oxygen content, so that metallic iron remains, one may say that the iron is reduced out of the iron oxide. This might be brought about by placing the iron oxide in contact with a substance which has a strong "desire" to combine with oxygen. For example one can heat up the iron oxide in a stream of hydrogen gas. This takes the oxide away from the iron oxide to form water, then the water is driven off and metallic iron remains. One of the commonest reducing agents is carbon, and iron may be prepared by heating iron ores such as the oxides with charcoal in an oven or furnace. A still more powerful reducing agent is the metal aluminium. This fact has been used by Dr. H. Goldschmidt for an industrial process of reducing metals from their oxides.

This process is called *aluminothermy* and since its introduction in 1897 it has come into wide use. To get the reaction started a very strong heating of some point in the mass is necessary. The mass consists of a mixture of aluminium with the oxide that is to be reduced, both in the form of a fine powder. Just as a match must be lighted, one must first heat a little portion of the material with an ignitor. This is globular and is called the firing-ball. It is placed nearly in the center of the mass. This method of firing the mixture is the most important detail of Goldschmidt's method. Sainte Claire Deville and Wöhler previously had tried to use aluminium for reductions with but little success. The firing-ball consists of a mixture of aluminium with the oxidation agent, barium dioxide, which takes the place of the potassium chlorate in the head of a match. To light this firing-ball a strip of metallic magnesium, which burns very readily, is fastened upon it. Magnesium, because it burns with a brilliant light, is used for the "flash-light" of photography. If for example, the composition of the mass consists of a mixture of aluminium and chromium oxide in correct proportion, then this mass will catch fire from the firing-ball and the chromic oxide will give its oxygen to the aluminium, which changes to aluminium oxide, also called *alumina*, Al_2O_3, while chromium metal is freed. At the high temperature which results, the alumina is melted to a slag-like mass called *corubin*. This latter is a substance of even higher value in trade than emery, which is a form of alumina that occurs in nature and is used because of its hardness as an excellent abrasive, for example as emery-wheels. The chromium metal obtained in this way may be used as an addition to steel and it gives a particularly hard body known as *chrome-steel*, of great usefulness. By this process large masses have been prepared of the valuable metals, chromium, cobalt, manganese, molybdenum, nickel and tungsten. In the case of the last mentioned the temperature of reaction is increased by passing air through the mass. It had never previously been possible to prepare some of these metals in a carbon-free condition, the chromium and the

manganese for instance. The presence of carbon greatly reduces their usefulness. Other bodies which the metallurgist finds difficult to prepare, such as titanium, silicon and boron, can be obtained by the aluminothermy process in the form of alloys — commonly with iron or copper.

Another use for this process is in welding iron and steel objects. If for example one wishes to weld together rails or repair a broken place in a rail the surfaces which are to be welded together must be jointed closely to one another and surrounded by a form of sheet-iron lined with corubin. A pulverized mixture of iron oxide and aluminium called *thermit*, is placed in a conical funnel closed below with a tap-hole. The thermit is fired and the melted mass is run into the sheet-metal mould by opening the tap-hole. The mould fills first with the molten iron which is heavier — afterwards the corubin slag flows out over the welded place. By the great heat both the rail-ends are expanded so that they press powerfully against one another. After the whole becomes cool the welded joint is polished off. In a similar manner broken iron and steel objects such as cog-wheels and propeller shafts can be mended without the necessity of transporting them to a workshop. Gas and water pipes can be welded together in this same way.

Oxidation and reduction agents play an outstanding role in the whole field of chemistry. The most important oxidation agent is the oxygen of the air. Pure oxygen separated out of the air has a still stronger action. Ozone has even stronger activity — it may be considered as "condensed" oxygen. It is used as a bleach and as a disinfecting material. All bodies which easily give off oxygen act as oxidation agents. Among these are nitric acid and its salts, for example ordinary saltpeter (potassium or sodium nitrate) used in gunpowder. Potassium chlorate acts in the same manner. Close to ozone stands hydrogen peroxide, H_2O_2, which is employed in solution, while the salts named above may be used in the dry condition at high temperature. Manganese dioxide, MnO_2, is also much used both wet as in Leclanché cells, and also at high temperatures.

Potassium permanganate is used in solution. Barium dioxide is also a powerful oxidation agent, much used both at low and high temperature. Chromic acid, commonly mixed with sulfuric acid, also serves as a powerful oxidation agent. Such oxidizers as ozone, hydrogen peroxide and potassium permanganate are used in medicine to destroy ill-smelling substances and micro-organisms.

Beside oxidation agents stand chlorinating agents. Hydrogen gas can burn with a flame in chlorine just as in oxygen. Hydrogen chloride is formed, while in oxygen or air, water is formed. Similarly illuminating gas will burn in chlorine with a ruddy, very sooty flame. Thin leaves of copper or tin-foil if they are dropped into chlorine burn with lively sparking to copper or tin chloride. Hypochlorites, which are obtained by leading chlorine into a solution of alkali, for example potassium hydroxide, can act both as chlorinating and as oxidation agents. They are used as bleaches and as disinfectants. Best known among them is chloride of lime. With the carbonic acid of the air, or other weak acids this gives hypochlorous acid, HOCl, which easily splits up into hydrogen chloride and oxygen and so has a strong oxidizing action. With hydrochloric acid it gives chlorine, which is a powerful bleach and disinfection agent. Chloride of lime is prepared by leading chlorine gas into slaked lime and is a yellow white powder with a strong chlorine odor. It is manufactured in great quantities. When chlorine is removed from a chlorine compound, the process is also called reduction, and to effect this a great many of the same bodies can be used which take oxygen out of oxides, i.e., reduction agents. The oldest and most used reduction agents for high temperature work are carbon, carbon monoxide and hydrogen gas. The metals magnesium, potassium and aluminium act still more powerfully. In solution the metal sodium is used as an amalgam, i.e., dissolved in mercury, also zinc and iron may be used in powdered form. A great number of chemical compounds themselves of a low degree of oxidation, such as sulfur dioxide, hypophosphorous acid, oxalic acid, hy-

droxylamine, aldehydes, and ferrous salts are much used as reducing agents. With these also stand hydrogen sulfide and stannous chloride (in alkaline solution). Of the highest industrial importance is the Sabatier method of reduction, whereby liquid fatty acids for example such as oleic acid may be "hardened," i.e., converted into solid fatty acid of greater worth such as stearic acid. This process depends on the use of finely divided nickel (or other metals) as catalysts. They are heated in a stream of hydrogen gas and fatty vapor, whereupon the hydrogen combines with the fatty bodies to be reduced. This method of "hydrogenating," i.e., of combining a body with hydrogen, is of extraordinarily great industrial value and also has great importance in the field of organic chemistry.

When an electric current is allowed to pass through a solution or melt, any metal present will wander to the negative pole which thus takes on reducing properties, while oxygen or chlorine will wander to the positive pole which thus becomes a place of oxidation. This fact has great importance both in industry and in the pure science. The positive pole can serve as a powerful oxidation agent, while the negative pole acts as a similarly powerful reduction agent. The power of the electrodes to oxidize and reduce increases with increased electromotive-force (potential difference) between the poles. In this way hydrogen gas for example can be reduced out of water, aluminium out of bauxite, magnesium out of carnellite which is a double salt, $KMgCl_3$, potassium chloride with magnesium chloride, found in the alkali salt mines. All these products are powerful reducing agents. At the opposite pole in the same way chlorine or oxygen may be obtained from sodium chloride or water respectively, and potassium chlorate from potassium chloride. Similarly hypochlorite which has great use as a bleach can be prepared electrolytically from a water solution of common salt, furthermore electrolytic oxidation can give lead peroxide, persulfates and chromates which are all powerful oxidation agents. Thus the electric current has become our most general and our foremost oxidation agent as well as reduction agent.

Chapter IV

TOOLS AND METALS

Fire, the first chemical agent of man, has been in use for sixty thousand years according to the calculations of Osborn. In the famous cave-dwellings of that early period at Krapina in Croatia, Dr. Kramberger Gorgjanovic has uncovered, among the many layers, one which consists of a great fireplace with a mixture of broken human bones, no doubt the remains of a cannibalistic banquet. At an even earlier time than this, man seems to have made use of mechanical tools. Darwin relates how an ape kept in a zoo used a stone to crack nuts that were given to him. After using this stone he carefully hid it away under the straw of his cage. This was therefore a tool, and undoubtedly the most ancient men, like the man-like apes, used similar tools to be found at hand in nature. The higher intelligence which distinguishes man from the animals most nearly related to him, has its origin in the fact that man works natural materials into tools for his use. In flint he found a material which on splitting gave sharp-edged pieces that could be used as knives, saws and drills. From the moment when he first made flint tools Paleolithic time begins and the oldest division of this age is called Chelles-time, named after the little town of Chelles in the department of Seine-et-Marne, near Paris. Chelles is well known, not only for its prehistoric deposits, but also as the residence of the Merovingian kings in later times. In that town are found a great number of sharp flints and many bones of animals upon which traces of human work are plainly evident. Osborn calculates that they come

Fig. 12. Early Work with Edged Tools
Head of a mammoth carved on reindeer horn.

from a time which lay from 75,000 to 100,000 years before our day and probably in a period between two ice ages, when the need of fire was not as great as it was in the Krapina period, which was concurrent with the last ice age. Thus it can be seen that the use of mechanical tools is older than the use of fire by man. Figs. 12 and 13.

FIG. 13. CARVINGS OF BULL AND COW BUFFALO ON REINDEER HORN

Flint lends itself to use for tools because of the sharpness of its edges. Flint is an amorphous, which is to say a non-crystalline, substance. Amorphous substances, of which glass is best known, are characterized by a shell-like, or scale-like, mode of fracture, and as a result of this the edges formed by the fracture are very sharp. That is why one can so easily cut oneself on bits of broken glass, while pieces of the coarsely crystalline rocks, such as granite, are not at all dangerous when broken. In primitive times men sometimes used a true glass, volcanic in origin, called *obsidian*, for making edged-tools, and because of the traditional age of such tools, the Jews, today, use knives of obsidian for religious purposes. Flint also possesses the necessary hardness for use as a tool. It is very widespread, too, in its occurrence in chalk-formations all over the world.

The places where flints were to be found corresponded in the Stone Age to the mines of today, from which we get our source of tools — the metal ores. The most important of the flint deposits of Europe became the centers of early culture. Such were Grand Pressigny in Northern France, Spiennes in Belgium, Cissbury in England, and Kvarnby in South Sweden.

Culture slowly grew during the 90,000 years of Paleolithic time. Tools were made better and better and their use became more widespread, their forms more diverse. Animal-bones and horn also came into use for making lesser tools such as fish-hooks, needles, awls, etc. Finally the Neolithic age arrived

when man began to polish his stone tools, both for improvement of their usefulness and of their appearance. This age began about 7,000 years ago.

The first metals which man learned to make use of were doubtless those which occur in nature in metallic state. Among these are gold, silver, copper, (immense amounts of this metal are found native on the shores of Lake Superior in Northern Wisconsin). Free iron occurs in the meteorites and also in masses in Greenland, as found by Nordenskiöld. Because of its appearance and weight the iron attracted the attention of man, and he came to discover its property of highest value — its malleability. It could be shaped by hammering, and could be given a sharp edge, which would not break as did the flint tools. The Greenlanders today gather the bits of metal and make from them sharp-edged tools such as knives. Doubtless they did this long before iron was introduced from Europe by the Norsemen. But native metals, especially native iron, are rather scarce, so that the stone tools held their place until mankind learned how to prepare metals from their ores in comparatively large amounts by smelting. Then only did the Stone Age come to an end. The easiest of the native metals to use for tools was copper, for it occurs mixed in a rock matrix. It is necessary only to crush and wash this and then melt together the metal bits obtained in this way. Copper oxide, and also the carbonates of copper are ores which give free copper easily by smelting with charcoal. They occur widely distributed. Finally man learned how to work the copper ores which are commonest of all in occurrence — those which contain sulfur. Copper was used before iron, doubtless because of the fact that it is easier to melt, and more malleable. At a later date than copper, tin was made from its ore, called cassiterite, an oxide, which occurs in Germany, in Eastern Australia, in Cornwall, and in very large amounts on Banka Island in the East Indies. Doubtless man was bothered by the softness of this metal which hindered its use for edge-tools. But after a time he found that a rather small addition of copper to the

tin hardened it and made it a better tool material. Bronze was thus found — a most useful metal and it lent its name to the *Bronze Age*, which in Greece began about 5000 years ago.

Iron finally supplanted bronze. Iron ores are very abundant and among them some are very easy to smelt, such as bog-ore and the various other oxides of iron. Probably, in former times, the iron was prepared in the simple way still used by African negro tribes. From time to time better and better means were found for preparing the metal, which is rightfully called the king of metals. The Iron Age followed the Bronze Age in the ancient world after the latter had ruled but 800 years, so the Iron Age began 4,200 years ago. In Sweden, however, the Bronze Age ended only about 500 B.C. The iron industry in India reached a high state of development at a rather early date. A testament of this is the pillar of iron 7.4 meters long and weighing 55 tons erected in the 5th century A.D. at Kytub near Delhi, and still standing.

Iron is particularly remarkable for the properties of its alloys. The simplest of these, known for as long a time as iron itself, contains a small amount of carbon. Iron containing less than 0.4% of carbon is called soft iron, since it cannot be hardened noticeably by sudden cooling. It is therefore easily malleable. Hardened iron is called *steel*. The maximum of hardening is obtained when the carbon content is 0.9%. Steel is also malleable when hot. If the carbon content increases to over 2%, the malleability disappears and the iron is called pig-iron, or cast iron.

The technique of iron manufacture has been advanced by the work of men of many nationalities. One of the earliest outstanding names is that of George Agricola, often called the father of metallurgy. It is often said that the land which produces the greatest amount of iron is the mightiest. While this may not be literally correct, still it cannot be far wrong. In the 18th century, Sweden held the top position, then it passed to England, thence to Germany, and today the United States

leads the world in this production. In the following table developments such as the effect of the war, etc., are shown (figures in millions of tons).

	1907	1910	1913	1916	1920
United States	26.2	27.3	31.0	39.5	35.6
Germany	13	14.8	19.3	13	6.2
Great Britain	10	—	10.7	9	7.8

In 1500 the world production was about 0.05, in 1600 about 0.07 and in 1700 about 0.1, 1750 0.2 million tons. In 1800 it had increased to 0.8, in 1825 to 2.0, 1850 to 4.8, 1870 to 11.6, 1890 to 27.9, 1900 to 41.2, 1907 to 61 and 1912 to 72 million tons and had dropped in 1920 to 40 million tons. It was highest at 77 million tons in 1913 and has dropped off since that date through the war period.

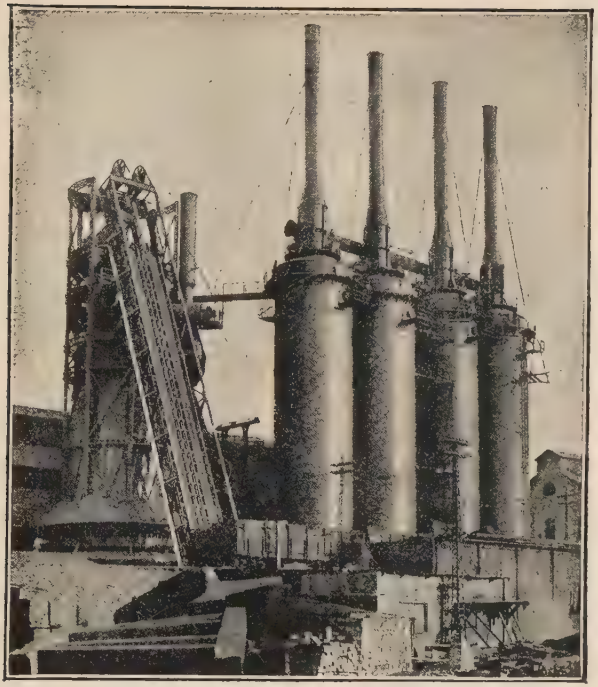
Growth has been so remarkably rapid that fear has arisen that the ores of iron will shortly be exhausted. At the eleventh International Geological Congress in Stockholm in 1910 this problem was given serious consideration, for the first time, and Professor Sjögren gave a survey of the opinions which have been expressed regarding this matter. He concluded that the known deposits of iron ore contain 10,000 million tons of iron. At the present rate of use this amount would only last 140 years. Since, however, it is very probable that the use of iron is still rapidly increasing this period of time must be made shorter, so that perhaps iron will not last till the end of this century. On the other hand all iron deposits are not yet known, possibly larger supplies than these known today are still undiscovered. On grounds too complicated to explain here, Sjögren calculated that the better prospected parts of the world, Europe, except for a few Balkan States, the United States, and Japan, possess known iron ores corresponding to seven thousand million tons of iron and a probable reserve of about 7 times this amount. If a similar distribution of iron ores can be looked for in other less well prospected parts of the world, the probable iron ores of the entire world corre-

spond to an iron content of 425,000 million tons. But this calculation is a very rough approximation, so that the world supply of iron really deserves as much attention as its supply of coal. In the case of the latter, there can be a certain replacement by the development of water power, the use of peat supplies, etc., in temperate zones, while in the tropics the sun's heat may come to be used to drive machines. But about the metal situation we can only say that man will soon pass from the Age of Heavy Metals to the Age of Light Metals. The light metals, and above all aluminium in the form of its alloys will then replace iron and steel. Certain alloys of aluminium and magnesium possess great strength despite their light weight, and in fact these were used in war days for Zeppelin framework, and for metal aeroplanes.

We may certainly conclude that in a comparatively short time man will be forced to content himself with poorer iron ores, (and today cheaper ores), than are considered worth smelting at present. Such poor grades of ore are to be found in Europe in the form of the minette ores of Lothringen, Luxemburg and France. Doubtless consideration of the value of these districts was a contributing factor in the causes of the world war. It is rumored, not without basis, that the desire for iron ores was the principal cause of the Morocco crisis of 1904, which threatened at the time to precipitate a world war. It is of interest to examine the distribution of the world supply of these ores low in iron, (magnetites and hematites). Such occur in the United States, in Brazil, Middle and Southern Africa and in India. In the tropics an ore known as laterite is very widely distributed.

The supplies of rich ore of more than 60% iron are very small. As far as known they can give 850 million tons, but there is reason to believe that further prospects may increase this figure, at most to about 1300 million tons of this valuable material. We may expect the price of such ores to rise sharply soon, as a result of the dwindling supply. Sweden has the good fortune to have within her territory two-thirds of the supply

PLATE II



From Roger's "Manual of Industrial Chemistry."

THE WORKSHOP OF THE AGE OF HEAVY METALS

A blast-furnace with its attendant set of pre-heaters. Since the fuel and the ore do not often lie in the same district each of them are brought half-way. Thus Lake Superior ore meets Pennsylvania coal at Gary, Ill., or at Buffalo, N. Y. In Sweden, where ore, water power and forest all lie together, iron is smelted in electric blast furnaces, in which wood charcoal reduced the ore to metal, but hydroelectric power furnishes the high temperature for the reaction.

of these rich ores. For the most part it lies in the ore deposits of Lapland (Norrbotten).

The alchemists' dream of transmutation depended on observation that when metals were treated with other substances their properties changed remarkably. Sometimes the changes required the introduction of only a very small amount of foreign substance. Changes of color particularly occupied the attention of the alchemists. They noted that red copper was altered in color to a yellowish green by taking up a comparatively small amount of zinc (forming brass) and that a very little arsenic would make the copper silver-white. The alchemists considered these metals to have been ennobled by these changes of color. We pay attention now-a-days more to the properties of a metal, such as malleability, castability, ductility, hardness, elasticity, tenacity, electrical conductivity and magnetic properties. The high value of bronze depends on the change in castability and hardness acquired by soft copper on addition of a comparatively small amount of tin. Sometimes small amounts of impurities are very undesirable. Thus a very slight content of phosphorus in iron makes the latter brittle at room temperature. A little sulfur makes iron brittle at red heat, so that in hammering or forging it may break. This latter undesirable feature can be decreased by adding manganese. The high value placed upon Swedish iron and steel, and the fame of the Swedish industry in the 18th century depended on the low phosphorus content of the Swedish ores and the freedom from sulfur of the wood-charcoal used in the smelting process, in place of coke. The resulting product is free from phosphorus and sulfur. The metallurgists of France sought in vain to lessen this difficulty in the French steel production; among them was the famous physicist, Reamur. For a long time foreign lands were dependent upon Swedish iron, if fine products were to be manufactured. Today this problem is solved, and Sweden's golden age is ended.

Iron, as it comes from the furnace, is raw or cast-iron and its carbon content is from 2.7 to 4%. It also contains between 2

and 3% of silicon, and this lowers the solubility of the carbon in the iron with the result that, on solidifying of the metal, part of the carbon separates in the form of fine grains of graphite. Gray cast-iron results in this way. Manganese acts in the opposite way from silicon. With lower silicon content or in the presence of manganese the so-called *white-iron* forms, this holds in combination its carbon content when it solidifies. Such iron is very hard and unlike gray cast-iron, can be worked with the file only with difficulty. It is more difficult to forge and not as easy to cast as the gray iron. Besides the impurities already mentioned, pig-iron may contain also phosphorus and sulfur, and these do not detract in any noticeable way from the good properties of these irons for casting purposes, indeed in a certain degree they are even favorable.

If malleable iron or steel is to be made from cast-iron, the content of carbon must be decreased. This is brought about by the process of fining whereby the manganese, carbon, and silicon are burned out. If phosphorus and sulfur are also to be removed, the slag must be "basic," that is to say it must contain only a little silicic acid and more lime and ferrous oxide. In the Bessemer process the converter in which the fining occurs has a lining of lime stone. The basic slag combines with the phosphoric and sulfuric acids formed by oxidation during the process. A high sulfur content is difficult to remove. In such case the slag must be kept basic even in the blast furnace and the temperature raised; thus the greater part can be removed. Phosphoric acid is of great value for the nutrition of plants so slags obtained from ores which contain phosphorus are used as valuable fertilizer material.

If the fining is continued only to a given degree, the amount of carbon necessary for *steel* can be left in the metal. Steel can also be made by adding the proper amount of carbon to malleable iron.

We must now consider the alloys of iron. An alloy with silicon, called *ferrosilicon*, is used as an addition to pig-iron to make a good grade of cast-iron. The silicon takes from the

pig-iron traces of oxides (carbon monoxide) which would cause the formation of blow-holes in the castings, if left. A very good steel for the manufacture of cutting tools contains 1.28% silicon, 1.2% carbon and 0.91% manganese. A low content of silicon is desirable for better quality cast-goods, and is often specified for steel for armament, and gun-castings. Thus, for example, the Krupp crucible steel used for gun-barrels contains 0.25 to 0.4% of silicon.

Aluminium has been proposed in place of silicon in cast-goods by Von Wittenstrom. However, too great an addition of silicon, and even less of aluminium, are undesirable, and to be avoided. In connection with his researches on iron alloys Hadfield sent to Prof. Barrett various samples of aluminium irons and silicon irons. The latter investigator with Brown, studied their electrical and magnetic properties. It was found that an iron with a content of aluminium of 2.25% had the lowest hysteresis of all irons investigated, this value being but two-thirds of that for the best Swedish iron. Since hysteresis losses are undesirable in electric instruments, especially transformers, the use of this kind of iron effects a great economy. The value of this alloy is also increased by its very great electrical resistance, so that the formation of the so-called Foucault currents, which cause energy losses in electrical machines, is hindered. Also of value is its high magnetic permeability, greater even than that of white iron, and this permits the use of smaller iron cores in electromagnets than would be required if they were made of soft-iron. Rather similar properties are possessed by an alloy of iron with 2.5% of silicon, so this and the aluminium iron have found widespread use in the manufacture of electrical machinery, (first in the U. S.).

Manganese steel is of particularly great value. In 1773 Rinman found that the addition of manganese destroys the magnetic properties of steel. A manganese steel with a low manganese content was first introduced into commerce by Henderson of Glasgow in 1876. At nearly the same time the Frenchman, Brustlein, was experimenting with steels of high

manganese content and he found these to have remarkable properties. The alloys were so hard he believed they could not be worked mechanically, so he considered them of no practical use. Meanwhile, Hadfield pointed out that the maximum hardness results from a content of 5–6% manganese. If the manganese content is made larger than this the hardness decreases till it approaches a minimum from which it again rises, only reaching the same high value as at 5% when the manganese content is 22%. It is the steel of manganese content around 12% which possesses the most desirable properties. This steel has no magnetic properties.

At a white heat ordinary steel and iron are almost unmagnetic. During cooling they begin to glow of themselves at about 760° C. (1400° F.). This phenomenon is called recalescence, and it indicates a chemical change going on in the iron. As a result strong magnetic properties appear. In manganese steel the recalesence does not occur. Thus the iron in such steel remains in the same unmagnetic state as at white heat. Also the electrical conductivity is lower; it is about one-eighth of that of ordinary steel and one-fiftieth that of copper.

For a better understanding of these properties of manganese steel, (and as we shall see they are also to be found in certain nickel steels), we must briefly discuss the changes which take place in iron on cooling. Pure iron melts at 1520° C. (2768° F.). If we cool from solid iron at a temperature near to the melting point, a change occurs at 1420° C. (2588° F.) and this is made evident by a period in which the cooling is slowed down, as has been demonstrated by Tammann. It is also displayed by a change in magnetic properties, as has been shown by Curie, Ruer and Schüz. On further lowering of the temperature two more changes occur, which are evidenced by changes of properties of the iron. One of these occurs at 898° C. (1652° F.) and one at 767° C. (1412° F.). If the iron is heated up again the changes occur in reverse order at 767° and 910° C. (1670° F.) and the previous condition is again arrived at. The change at 767° is considered to be reversible, that at 898° and 910° is irreversible,

for it occurs at different temperatures depending on whether the temperature is rising or falling. The above is for pure iron. If now carbon is introduced into the iron, a new transformation point appears at a somewhat lower temperature, but at the same time the two other transition points begin to approach each other, so that when the carbon content reaches 0.4% they both occur at 767°. Below this temperature such iron has magnetic properties, above it none. If the carbon content is increased still further, then with 0.8% C. all three of the transition points lie together at 695° (1283° F.). If manganese or nickel are now also added, this common point of change is still further lowered, and becomes more irreversible so that alloys of 12% manganese or 25% nickel remain almost unmagnetic when cooled to room temperature. Hardening (in water) acts on this manganese steel in quite a different manner from upon ordinary steel, for the latter is made brittle by such treatment. The ductility of manganese steel on the other hand, increases under such treatment, from about 30–40% to about 40–50% without the appearance of cracks and flaws. By adding nickel to this manganese steel, the ductility can be increased to 60–70% so that this steel possesses a high degree of strength to withstand breaking under blows, and, on the other hand, its ability to withstand abrasion is very high because of its hardness. All these properties have been contributing factors to the use of such steel for machine parts, which are planned for heavy mechanical work, and for railway rails in stretches where they must withstand hard usage.

Alloys of iron with nickel have also remarkable and useful properties. The first of such alloys were prepared by Stodart and Faraday in 1882. By 1885, these alloys were being manufactured on an industrial scale in France. In 1889 Riley noted an extraordinarily valuable mechanical property of steel containing up to 49% of nickel. Hopkinson, in the same year found that a steel containing 25% nickel was almost without magnetism at temperatures up to 700° and 800° and that it showed no recalesence on cooling from these temperatures.

However on cooling somewhat below 0° such steels took on magnetic properties and these were still more marked when they were cooled to −50° (−58° F.). The steels retained this magnetic property on heating as high as 580° C.; at this point they lost this ability, and magnetism did not return on cooling to room temperature. So we see that such steel exists at ordinary temperatures in two modifications, one magnetic and one nonmagnetic. One of Hadfield's test steels containing 25% nickel, 5% manganese and 0.6% carbon, the rest being iron, was found by Barrett and Brown to show the lowest electrical conductivity of all iron alloys which had then been investigated. Its electrical conductivity was 60 times less than that of copper. Hopkinson found that the electrical conductivity of 25% nickel steel at 160° C. (320° F.) was 19,200 for the magnetic form, but was only 13,900 for the nonmagnetic form. It may be stated for comparison that pure iron according to Benedick's figures, has a conductivity of 130,000 while the figure for cast iron is around 24,000 and for ordinary steel around 30,000. The latter figures vary considerably depending on the composition of the cast iron and of the steel in question. Mercury has a conductivity of 600,000 at 18° C. (64° F.). According to Burgess and Aston nickel steel with about 34% nickel, corresponding to the formula Fe_2Ni, has the lowest conductivity, at about 11,600. That the alloy Fe_2Ni is an actual chemical compound also appears probable from the magnetic and thermal properties of such steel, studied by Osmund and Weiss and by Guertler and Tammann, and also from Chevenard's investigations of its density. This latter value indicated the presence also of the chemical compound $FeNi_2$. The ductility and the elastic limits both have a maximum at about 18–20% nickel content. At this point they are about 5.3 times the ductility of iron, and 9 times the elasticity (with the carbon content constant at 0.2%). In 1895 Guillaume found that the heat expansion of a nickel steel of about 30% nickel content is very low (between 0° and 38° C.). It is only about one-third of that of platinum, which has the

lowest heat expansion of all the pure metals. The lowest figure for the heat expansion is at 24% nickel (corresponding to Fe_2Ni), and at this point it is only one-seventh of that of platinum. By the addition of one percent of manganese or chromium, Guillaume succeeded in making alloys that actually contracted on warming. (They contained about 40% nickel). So by choosing the right combination it is possible to make from such alloys wires or bands which do not change their length with changing temperature. These have found use for the manufacture of the measuring tapes used in geological measurements. Bars of such metal are used for the pendulums of clocks.

In general the elasticity of a metal decreases with increasing temperature. Guillaume found that nickel steel behaved in quite the opposite manner, within the range of the irreversible change between the two modifications. Possibly this is due to a change occurring very slowly. In this way springs can be made, whose elasticity does not noticeably change with temperature. Such springs are used in the balance wheels of precision chronometers. The metal which does not expand on warming is called "Invar" (unvarying). It contains about 36% nickel, 0.5% carbon, and 0.5% manganese. At temperatures under 200° C. it changes very slowly, and it is therefore aged before use by warming it gently for some time. It can be forged, rolled, polished, and drawn into thread, or wire, and can take a beautiful polish. Steam harms it very little; it is not likely to rust. It is manufactured on a large scale because of these useful properties. In the field of nickel steel manufacture the Commentry-Fourchambault Co. has been foremost in investigation. This company backed the researches of Guillaume.

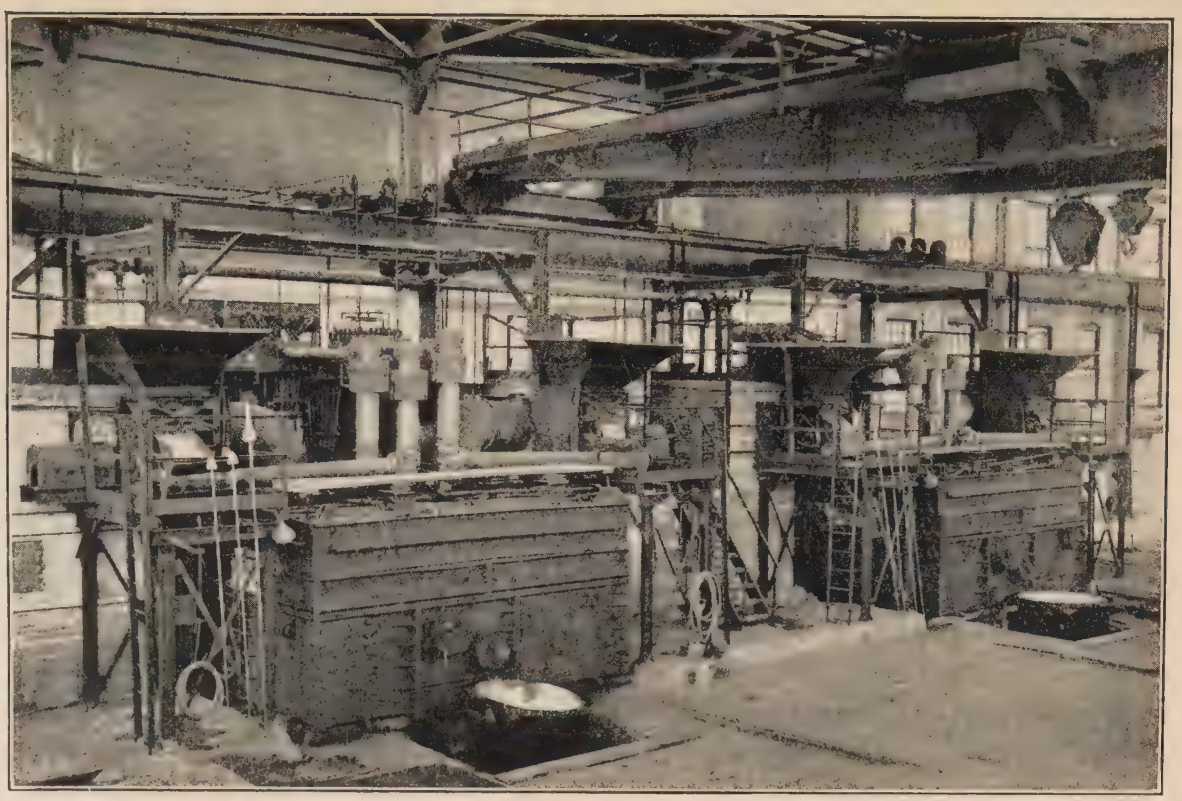
Nickel steel of 0.8% carbon content and with less than 5% of nickel is remarkable for its high coefficient of elasticity and for its tensile strength. It is used for armor plate, cannon, large axles, auto parts, and in steel-frame buildings. If the nickel content is high, 5–15%, the elasticity and tensile strength are lower, but the hardness increases. Such steel takes a good

polish and resists oxidation. As it has higher elasticity and tensile strength than has ordinary steel of the same hardness, it is an improvement on such steel.

If the nickel content increases beyond 15% the steel can withstand powerful strain without breaking. It is used in machine parts which are to receive sharp blows. Invar belongs to this group, and other alloys which are also remarkable for their small volume, change with change of temperature, as well as for special elastic properties. Invar is used for the degree-scale of measuring instruments in which constancy of length is important, for rules, for chronometer balance wheels, and also for the tubes of steam boilers. An alloy with 46% of nickel has the same expansion coefficient as platinum and therefore it is called *platinite*. It is used in place of the more costly metal in incandescent lamp manufacture. It is also used for the settings of lenses in optical instruments. The high electrical resistance of the alloy with 25% nickel, together with its slight change with temperature, have favored its use for the manufacture of electrical resistances.

On the whole one can say that nickel steels have been extremely important both for industrial and for scientific purposes. If instead of nickel we add chromium to a steel it increases the hardness, but decreases the malleability, and the weldability of the steel. *Chrome steel* is used for the manufacture of projectiles, which must have great penetrability, and also is used for cutting tools and for articles which are to receive heavy friction. Also it is used for the protective screens for guns, for steel helmets, as well as for the equipment and armor of battleships. In regard to cheapness and strength it surpasses tungsten steel, but it generally cannot compete with manganese steel.

Chrome steel containing from 10 to 14% of chromium does not easily rust. Steel which contains any considerable amount of tungsten is extremely hard, but is also brittle. Therefore it cannot safely be used for tools which will receive blows. But this disadvantage is sometimes offset by the fact that tools



Courtesy of the Vanadium Corporation of America

AN ALLOY-STEEL WORKSHOP. ELECTRIC FURNACES FOR THE PREPARATION OF VANADIUM-STEEL.

Vanadium-steel alloy today constitutes one of the most important of materials for automobile and airplane parts. It is remarkably tough so that rods of it can be bent double without breaking. Carbon-vanadium steel makes excellent tools. Chrome-vanadium steel is used for automobile springs. Almost the entire world supply of vanadium comes from deposits in Peru, near the summit of the Andes. The ore is called "patronite," a vanadium sulfide.

prepared from it can withstand higher temperatures without losing their hardness, so that the cutting power remains good. *Tungsten steel* is used in machines that drill and bore, where at a rapid work-pace the cutting parts are liable to become greatly heated. For this reason tungsten steel is sometimes called "quick-boring" steel. In such steel there is commonly present also from 3 to 4% of chromium and about 1% of vanadium. This steel, which brought about a revolution in machine-shop practice, was discovered by the Americans, White and F. W. Taylor (the "Taylor" system). Steel containing over 3% molybdenum has properties similar to tungsten steel but is less brittle, though ordinarily more expensive. Molybdenum and tungsten are closely related chemically. They belong, as does uranium to the chromium group of metals. During the war the price of tungsten in many countries became so high that molybdenum took its place.

The commonest metal, next to iron, is *copper*. This had not long been in use before it was learned that the addition of tin up to 10% increased the tensile strength and hardness and so made the metal more useful for the preparation of tools. This alloy, *bronze*, is noted, as above stated, for its greater usefulness than copper for castings, being easier to melt. In general the melting point of a substance is lowered by the presence of foreign substances. The difficulty of trying to cast copper is that the metal in molten condition can take up various gases, oxygen, carbon dioxide and sulfur dioxide, and these, when it solidifies, are released, make the metal porous and cause blow-holes. This property is counteracted by the presence of other metals. Hence the greater value of bronze. Bronze can also be hardened by slowly cooling it, while after rapid cooling it is soft and can be forged. The usefulness of bronze is known to everyone. The oldest objects of the Bronze Age contained only a slight amount of tin. This has been increased up to about 10%, the latter figure representing the bronze used modernly for guns. The very oldest bronzes often contained various amounts of other metals, especially lead, and even arsenic,

antimony and iron. The low tin content probably indicated the scarcity of that metal at the time.

Bells must consist of a hard metal in order to withstand the blows of the clapper. On the other hand the hardness must not be too great for good tone. For *bell-metal*, therefore, a bronze is used which contains between 20 and 23% of tin. Still higher tin content, about 33%, is used in mirror-metal, which was used in ancient times, and is used today in the Orient, for the manufacture of mirrors. The important property here is the ability to take a high polish, and not to scratch easily. This goes hand in hand with hardness. Addition of a little lead or antimony appears to be advantageous in this respect. *Mirror metal* was made in Roman days chiefly at Brundusium (now Brundisi). Hence came the term "aes brundusium" that is to say, Brundusian copper for mirrors, and from this expression the word "bronze" was later derived. The commonest usage of bronze today is for coinage and for art-castings. The added metals serve the purpose of increasing the hardness in order to lessen the wear of the coin. Art-bronzes which have been used from an early time, must have the properties of being easy to melt and cast, they must fill out the mould well and be free from blow-holes as well as easy to work and capable of withstanding the action of the air. In this latter regard it is advisable that the color changes which occur with surface-oxidation shall be pleasing to the eye. On this account the presence of any considerable amount of zinc, or the presence of arsenic is undesirable in art-bronze. The copper content is commonly around 86%, tin 7%, the remainder being zinc and lead in about equal proportions. Bronze is used in machine-work as a *bearing metal*. Such bronze contains about seven to eight times more copper than tin, and a larger amount of zinc up to about 8%; this is because zinc decreases hardness. Often there is added to bearing-metal bronze a little manganese, at most 0.5%, to remove the oxides of tin and copper and so to increase the tensile strength. As the manganese content increases the material takes on a white color with a ruddy

PLATE IV

THE CULTURE-CHEMISTRY OF ART BRONZE. JAPANESE BRONZE VASE, 19TH CENTURY.

The George Walter Vincent Smith Collection,
Art Museum, Springfield, Mass.

tinge and will take a beautiful polish. An alloy of copper, zinc and manganese is often used in place of German-silver.

Instead of manganese, phosphorus can be added to bronze to clear it of oxides. Since the presence of phosphorus in a bronze lowers its tensile strength, the phosphorus, in the form of a copper-alloy containing 10% phosphorus, must be added in just the right amount to remove the oxygen from the oxides during smelting. A product so obtained is called *phosphor bronze* and is particularly useful. It is used for machine parts which are liable to receive heavy friction and for articles which may come into contact with sea water, which acts much less upon this alloy than upon iron or steel.

An alloy with a main body of copper (50–70%) and a residue of zinc (20–30%) and nickel (10–25%) is called *German-silver*. This alloy originated in China, where it was called "pakfong" and used for all sorts of articles in place of silver, which it resembles in color. It has less lustre than silver and is not of a pure white, particularly if the copper content is great as compared to the nickel content. One cannot well use more than four times as much copper as nickel. The addition of iron, or, still better, of cobalt makes a German-silver whiter. This alloy is also noted for its great variation in electrical conductivity with change of temperature, so it was formerly used a great deal in the manufacture of electrical resistances for measuring purposes. In modern practice it has been replaced by other alloys, of which the most important are "manganin," containing 84% copper, 12% manganese and 4% nickel, also "constantan" with 58% copper, 41% nickel and 1% manganese, and "nickelin" with 54% copper, 25% nickel and 20% zinc. Although the electrical resistance around 0° C. in the case of a pure metal increases 4,000 million units for each degree, the change in the case of German-silver is 370 million, for nickelin 200, for constantan 30, and for manganin lower, 20 million units for each degree of temperature. In the electrical industries, which are of continually growing importance, the two last-named alloys have found great use.

Another alloy of copper which has been known from very early times is *brass*, in which zinc is the added constituent. The higher the zinc content, the more does the red color of copper change to yellow, until with over 50% zinc it becomes nearly white (*white brass*). The hardness and the tensile strength also increase but the usefulness decreases as the zinc content increases. Brass is a valuable metal for castings and is used in place of copper for machine parts, for cooking utensils, for cartridge cases, and as plate, tube and wire. Its ability to withstand oxidation by the air contributes to its value. Its golden yellow color and high lustre make it useful for decorative objects. The golden lustre is increased if the brass is dipped for a short time in nitric acid and then polished. Brass with 15% zinc is sometimes used for the preparation of false gold leaf and of "bronzing" paint. Brass is worked and machined on a very large scale.

When the zinc content of a brass is below 35% it can be machined and drawn only at a low temperature and not when hot. An alloy with 40% zinc is called "New Brass" and has the advantage that it can be machined hot and so has been used a good deal for the sheathing of steamboats. This valuable property can also be increased by the addition of a few per-cent of aluminium. Such an alloy is called *Aluminium Brass*. An alloy of copper with 5 to 10% aluminium is called *Aluminium Bronze* and is quite hard and ductile and can be forged at red heat. It is remarkable for a beautiful golden yellow color, unchanging even at a glowing heat in air. Hence it is much used for household and ornamental objects.

Silicon bronze possesses similar properties. The addition of only 0.3% of silicon to copper lowers the electrical conductivity about 2%. In this case another technically important property of the copper is changed: its tensile strength is increased. Such a property is so useful for electrical conductors that the 2% reduction in conductivity can be exchanged for the 50% increase in strength. However, further increase in the silicon content causes a further decrease in conductivity and the alloy

becomes hard and brittle. In working silicon bronze planned for electrical conductors, it is therefore customary to start with pure copper and to add a carefully weighed amount of a copper-silicon alloy of known silicon content (ordinarily between 10–35%).

Copper furnishes one of the best examples of how the properties of a metal may be changed by the presence of very small amount of impurities. The most important use of copper today is in electrical conductors. It is valuable for this purpose because of its high electrical conductivity. If this is set at 100 for pure copper, the addition of but 0.05% of carbon lowers it to 80.5; a content of 0.87% of phosphorus drops it to 20.6; while 2.8% of arsenic carries it down to 14.12. From this list it is evident that it is mainly the non-metallic elements which produce great decrease of conductivity, but any metal is detrimental in effect upon this most important property of copper. Therefore it is of the greatest importance that copper should be freed from impurities. Nowadays this is done by electrolytic refining. This is a very advantageous method, for the impurities, which fall out as a mud below the anode, (the positive electrode), often contain substances of value, such as gold, silver and bismuth. In 1920 the United States produced 600,000 tons of copper. In 1908 the world production was 762,000 tons of which the United States furnished 430,000 tons, all the other American lands 130,000 tons, Europe 109,000 tons, Japan 44,700 tons, Australia 40,100 tons.

Gold was probably the first metal that man learned to recognize. The Egyptians of the fifth century B.C. had great stores of gold, and the gold reserves of Mycenae, in the second century B.C., are famous. The reason for the high place of gold in history, is its occurrence in nature in native form. It is often found in nature alloyed with other metals, particularly silver. This latter alloy was called *Elektron* and was much used by the ancients, especially for coinage. The famous Croesus of Lydia replaced the elektron coinage then in circulation by a

gold coinage, and this is an indication that the people of that time (550 B.C.) knew how to separate gold and silver chemically. Gold is malleable, and it can be drawn easier than the other metals, so that it can even be hammered out into the very thinnest of sheets, "gold-leaf." It is very soft and is often alloyed with copper to counteract this. An alloy with 10% copper is used for coinage in most countries (though not in England).

Silver seems to have come into use later than gold and copper, and it originally was worth more than gold. The hardness of silver is between that of gold and copper. To lessen its wearing away it is alloyed with copper. The United States produced 50 million troy ounces of silver in 1921. The production was highest in 1915 at 74.9 million troy ounces. The gold production of the United States in 1921 was 2.37 million troy ounces, while the high figure of 1915 was 4.88 million troy ounces. Silver has nearly the same use as gold. Both metals are often used as a shining and attractive coating for other metals. Silver salts are extensively used in the field of photography.

Mercury is very like in its qualities to the noble metals. It is not affected by air at ordinary temperatures and also it occurs in native form in nature. It has been known since about 400 B.C. The extraordinarily great role played by quicksilver in alchemy has already been discussed. Its alloys with other metals are called *amalgams*. These have some practical use — for example in the dental art. Amalgamation of zinc or of cadmium, or even other metals, is often made use of in the preparation of constant galvanic cells, used in telegraphy and in the electrical industry. Mercury is also used in many physical instruments such as barometers, etc.

Lead and *tin* were known long before the days of our calendar, tin probably first, because of its use in making bronze. The two metals were not distinguished one from the other. Tin was called white lead, and was often adulterated with lead, which was called black lead. Even antimony came under this general name, for it was said that antimony glance (the sulfide) on roasting with carbon gave "lead." Basilius Valentinus

in 1450 first distinguished between lead, antimony and tin. These metals are all notable for their low melting points, tin at 230° C. (446° F.), lead at 330° C. (626° F.) and antimony at 430° C. (806° F.).

Lead (or possibly tin) was looked upon by the early Egyptians as the most typical of the metals because of its ease of melting, for fusibility was considered as one of the important attributes of a metal. It was a necessary property for the preparation of large quantities of the metals. Thus this metal came to be considered as the primal metal, and was given the name of *Osiris*, after one of the chief gods of the Egyptians. When later quicksilver was discovered, it took the old role of lead as primal metal, for it was liquid at ordinary temperatures. Alloys of tin and lead were used from an early date. Tin can readily be prepared in leaf-form, (tinfoil), because of its softness. Some lead is ordinarily added in the preparation of foil, and in making vessels of pewter. *Antimony*, in contrast with tin is hard and brittle, if it is added to tin or lead it increases their ability to withstand friction. An alloy of about 85% tin, 2–5% copper and the rest antimony is called *Britannia metal*, and is used, either cast or pressed, for household utensils such as spoons, forks, pots, cooking dishes, etc. Lead is often added to this metal, but is dangerous to the health if used in any considerable amount in tin cooking vessels, so the amount is controlled by law.

An alloy of 70–80% lead and 20–30% antimony is used for *type-metal* which must be of low fusibility, yet not too soft. Because of its low melting point, tin is used for *solder*. For the same purpose there can be used a cheaper mixture of equal parts of tin and lead which melts at 240° C. (464° F.). By adding bismuth, alloys melting at still lower temperature can be obtained. *Bismuth* itself melts as low as 256° C. (492° F.). Among such alloys is *Rose metal*, which melts below the boiling point of water at 94° C. (201° F.) and consists of a mixture of 50% bismuth, 25% tin and 25% lead. *Wood's alloy* consists of one part by weight of tin, two of lead, four of bismuth and one

of cadmium, and it melts at 60.5° C. (141° F.). Lead has considerable use for pipes and in sheets, and has a special use in storage batteries. Bismuth belongs to the same chemical series as phosphorus, arsenic and antimony, and is closely related to these elements. It occurs in nature in the free state (for example at certain mines in Saxony), and because of its low melting point it is easily obtained by smelting from ores which contain it. It appears mottled on the surface on tarnishing, and has thus drawn attention to itself, being known since the 14th century. Another easily fusible metal is *cadmium*, whose melting point is 322° C. (612° F.). This occurs together with zinc ores, especially in Silesia. It is closely related to zinc. It is more volatile than the latter metal (it boils at 778° C. (1432° F.), zinc at 918° C. (1652° F.), so it can be distilled off, and separated from the zinc. Cadmium, which gets its name from the old Latin name, "cadmia," for the zinc ore, calamine, $ZnCO_3$, or zinc carbonate, was first discovered in 1818 by Stromeyer and simultaneously by Hermann. It is used in galvanic cells planned for electical measurements, and for the preparation of such alloys as Wood's metal. Its sulfur compound is a useful yellow paint called "Brilliant Yellow." A table is given of the melting points of the metals here discussed. In parentheses are figures for the impure metals as they occur on the market. The figure for copper is for its melting point in the presence of air.

Metal	*Melting Point*	*Metal*	*Melting Point*
Mercury	− 39° C.	Silver	954° C
Sodium	+ 97	Gold	1064
Tin	232 (228)	Copper	1084 (1064)
Bismuth	268 (260)	Cast Iron	
Lead	322	White	1075
Cadmium	322	Gray	1200–1275
Zinc	419 (413)	Manganese	1245
Magnesium	632	Steel	1350–1400
Aluminium	657	Chromium	1587

Platinum melts at 1770° C. Iridium at 2200° C. Molybdenum has a still higher melting point and the melting point of tungsten is far above all these metals (at about 3000° C.).

Zinc, today a particularly useful metal, was not known in the form of the free metal in Europe until after 1700. Long before, during the Middle Ages, it was known in India and in China, from which land it was introduced into Europe by the Portugese and the Dutch. Pieces of zinc imported in this manner from the orient were described by Paracelsus, and also were written about by Libavius (1595). Calamine, the zinc ore, was well known to the ancients, for brass was made by adding calamine to a copper ore and reducing the mixture to metal. The oxide, ZnO, used as a paint under the name of "Zinc White" is prepared by leading zinc vapor into the air, where it burns. This oxide was well known in the Middle Ages as "philosopher's wool" (lana philosophica). When zinc was first prepared in metal form it was thought that because of its brittleness, it was quite useless, but later it was found that the brittleness disappears when it is heated between 100° and 150° so that it can then be rolled or drawn into wire and modernly it is used quite considerably, particularly as sheet metal, for roofing, etc., and also for cast-ware because of its cheapness. Articles of ornament made of zinc are usually bronzed. Zinc is also used in the manufacture of galvanic cells, both the "dry" cells and the "wet" type.

Like aluminium it becomes coated on exposure with a thin coating of oxide which protects it from further action of the oxygen of the air. It is used for the galvanizing of iron, in considerable quantity (see page 54). Its alloys, brass and German-silver, have already been described here. Another useful alloy is the so called "delta metal" which contains about 56% of copper, 41% zinc and small amounts of manganese, iron and lead. Like brass it is a yellow metal, it takes a good polish, is hard and strong, and withstands oxidation by air or by acid vapors. Furthermore it is easily fusible and casts well, it can be drawn into wires and pressed at ordinary temperatures, and can be forged at red heat. So it has considerable use.

The last discovered of the metals which have assumed great importance in our culture was *aluminium*, first prepared by

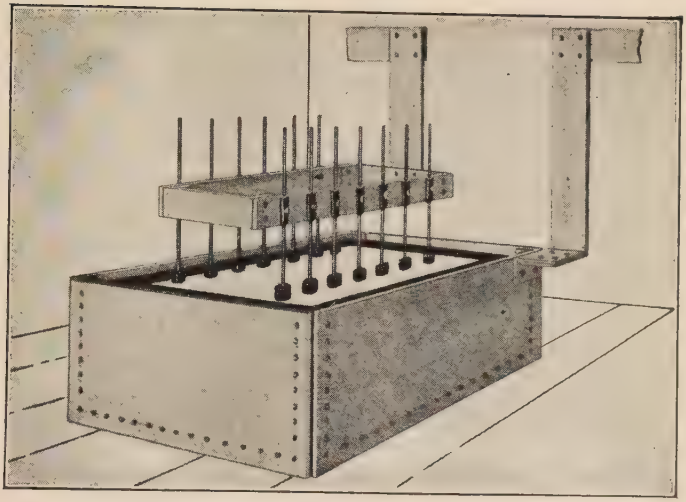
Wöhler in 1827. Nowadays it is produced on a large scale, and cheaply, by an electrolytic process. The mineral bauxite is the raw material (hydrated alumina). Aluminium is a very soft metal, the specific gravity is only 2.5, and so it is used for work which must be of very light construction — for example in airships. Its electrical conductivity is about 62% of that of copper, and because of the expensiveness of copper it is used for electrical conductors in place of that metal. Aluminium is acted upon readily by oxygen, and becomes coated with a film of oxide which protects it from further action by the oxygen of the air. If the metal is amalgamated this film disappears and it rapidly oxidizes in the air, with a great increase in volume. Aluminium is used in cooking utensils, but it must be kept away from alkaline liquids for they rapidly attack it.

A fine example of how greatly alloys may differ from the constituent metals is displayed by the alloy "magnalium," an aluminium with a little magnesium added (3-15%). Magnesium is a light metal very like aluminium, easily oxidized and becoming covered with an oxide coat in damp air. It is made electrolytically from carnallite, a double salt of potassium chloride and magnesium chloride, which is found in salt deposits. It has a specific gravity of only 1.74, so the density of the alloy magnalium is lower than that of aluminium. Yet the magnalium is much harder than aluminium and takes a finer polish than that metal. It is easily worked, and possesses greater strength than aluminium. Magnalium, despite the great affinity of its constituents for oxygen is itself oxidized less easily than is brass or German-silver — so one can see that it has quite useful properties. A metal of this sort, possessing considerable strength and yet of light weight, was used by the Germans for the framework of the Zeppelin airships. It contained:

Aluminium	95.04%	Silicon	0.24
Zinc	3.15	Iron	0.08
Magnesium	0.97	Carbon	trace
Copper	0.52		

Although it cannot be considered as one of the metals in

PLATE V



Courtesy of the Aluminium Company of America.

IN THE WORKSHOP OF THE AGE OF LIGHT METALS

An electrolytic pot for the preparation of aluminium from its molten ores, cryolite and bauxite. The molten aluminium collects at the bottom of the pot and is tapped off at intervals. The temperature of the bath is about 1000° C. The pot is lined with carbon. The electrodes are of specially prepared pressed and baked carbon. Various details of the furnace are not shown here.

general use in the metallic form, we may finally speak of *sodium*, for it plays a great role in chemical industry. Sodium is one of the constituents of common salt, whose chemical name is sodium chloride. In occurrence it is the commonest of all easily soluble salts. A few difficultly soluble salts such as the silicates and calcium carbonate (found as chalk and limestone) are of still more common occurrence in the rocks. Common salt is prepared from sea water, or from the water of salt springs, by evaporation, or it is mined from salt deposits. Sodium metal, is prepared by the electrolysis of sodium chloride or of sodium hydroxide, which latter is itself prepared by the electrolysis of sodium chloride in water solution. This method of electrolytic preparation was first used by Davy in 1807. Sodium is a shining, silver-white metal which oxidizes very rapidly in moist air (but much more slowly in very dry air) and it is ordinarily preserved under petroleum oil. Its specific gravity is 0.97 — lighter than water (sp.g.1.00). The metal is hard at temperatures under — 20° C. but at ordinary temperatures is soft like wax and can easily be cut with a knife. Its salts are of great importance in life. The most important, next to the common salt, is sodium carbonate, called *soda*, which we have already seen is the chief chemical handled in the chemical industry. Further important salts are sodium nitrate or Chili saltpeter, an important fertilizer, sodium sulfate or Glauber's salt, used as a raw material in Leblanc's soda process, and in the manufacture of glass, sodium sulfide and sodium nitrite used in the dye-industry, and many others. Soda-lye or sodium hydroxide is used for soap manufacture, and sodium sulfhydrate is used in the cellulose industry. Sodium itself is an indispensable and powerful reducing agent, used particularly in the field of organic chemistry in many processes of synthesis.

In 1807 Davy also prepared the metal *potassium* in an electrolytic way. It is very like sodium, melts at 62.5° and furnishes many valuable salts such as saltpeter, potassium chlorate, potash, potassium cyanide, potassium bromide, iodide, etc.

Like the breeding out of new races by the crossing of different

old races — new races which possess the valuable attributes of the parents but lack their weaknesses, and are thus of immense usefulness in the economy of living nature, both in the plant and the animal world — so the metallurgists by mixing various metals make alloys, which can possess widely diverse, desirable properties, and which supply products of extreme value for the advance of industry.

Chapter V

THE CULTURAL VALUE OF SILICA

For as long a time as man has made use of stone implements he has probably also made use of tools, manufactured of horn, bone and teeth of animals and from the bast or wood of plants. It was a simple thing to make use of the bones of the larger animals as a club or hammer. When it was discovered how to make knives of flint, it became possible to work bone and so to manufacture all sorts of objects such as needles, awls, fish-hooks, hoes, etc. Ivory was particularly desired for its hardness. Next to fire, stone and bone implements constituted man's most valuable aids in the earlier part of the Stone Age, the so-called Paleolithic time. During the period of transition from the older to the later Stone Age a new material was introduced — *baked clay*. In the Danish kitchen middens, which are collections of household refuse from the human habitations of that early time, and in corresponding layers from the whole latter half of the Stone Age fragments of extremely crude pottery are to be found. Probably the art of making objects of burned clay was discovered by chance from the fact that pieces of clay employed to wall-in fire-places became burned. After the burning these hung together and did not soften in water. Mankind had acquired a new and particularly useful material.

Fig. 14. Later-Stone-Age Bowl from near Zurich. Hand-moulded pottery.

The first clay vessels were doubtless made in the following manner: Clay, which occurs very abundantly in the earth's surface, was stirred up with a little water so that it became

plastic and could easily be moulded. It was beaten out by hand into thin slabs, then suitable pieces were joined and worked so that a vessel of desired shape would result. This was then fired or baked. This primitive method of preparation is still in use among various peoples in Africa and America. The invention of the potter's wheel took place at a much later date, probably in Egypt. With the aid of this tool the preparation of pottery was greatly simplified. That it was possible, however, to prepare beautiful objects without the potter's wheel may be seen from Fig. 14, a bowl from a lake dwelling near Zurich, Switzerland.

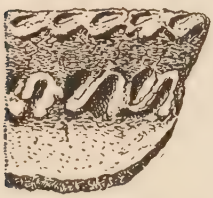


FIG. 15. FINGER-MARK ORNAMENTS ON POTTERY (ZURICH).

The making of pottery vessels has been of the greatest importance in the development of a sense of beauty in man, for undoubtedly clay objects were an incentive to the use of ornamentation. It was probably noted that the impressions from the fingers that resulted from working the clay were found to remain after firing and to be permanent. Next a pleasure was found in designing an ornament by applying such finger marks in a regular arrangement, see Fig. 15. Later it was preferred to make the marks needed for ornamentation of the clay by the use of pointed objects. A fine example of what could be made even in the stone age by means of this simple technique may be seen in Fig. 16, which is a picture, 1/6 size, of a clay urn found on the island of Moen in Denmark.

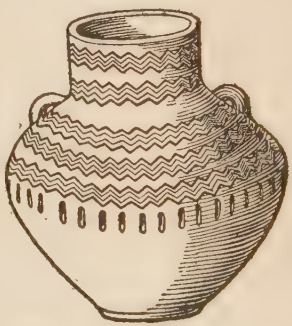


FIG. 16. STONE AGE URN (DANISH).

The silicates, or in other words the salts of silicic acid (p. 97), are bodies occurring most abundantly in the solid crust of the earth. They are of the very greatest importance to us, yet their chemical composition is comparatively little known. This is because they are in general

insoluble and poorly reacted upon by most chemical reagents. Also they are hard to fuse and they crystallize only with difficulty from their melts when these cool.

Clay in pure form is called *kaolin*. Its chemical formula is $(SiO_2)_2$, (Al_2O_3), $(H_2O)_2$, i.e. it is a compound of two molecules of silicic acid (silica, SiO_2) with one of aluminium oxide, Al_2O_3, (also called alumina) and with two molecules of water. Pure kaolin is white and is used in the manufacture of fine porcelain. It is formed by the weathering of felspar. At 500° C. (932° F.) the water content is lost and the kaolin partly decomposes into silica and alumina, which can dissolve in hydrochloric acid. To this is due the effect of burning or firing clay articles.

Common clay is gray because of the presence of organic substances. It generally contains iron, which is what gives brick its ordinary red color. The ability of the iron to color clay objects disappears in the presence of titanic acid. This latter alone gives the clay a disagreeable gray-yellow color after firing which lowers the value of the pottery. The presence of chalk in large grains is harmful because this on firing gives lime, which takes up water from the moisture of the air and causes the pottery to break asunder, for example in the case of bricks. The presence of free silica diminishes the red color due to iron. Gypsum in the clay gives a whitish bloom on the brick. Yellow clays are often found which contain an iron hydrate. Bauxite is a clay which gets its red color from iron oxide. Some clays are green because of an iron silicate, nontronite. Pure kaolin is very hard to fuse; it is said to be "fire-resistant." It melts at 1800° C. (3272° F.) but it bakes together at as low as 1400° C. (2552° F.). The melting point is lowered by the presence of impurities. Mica is to be found in nearly all clays. Its presence is advantageous for porcelain manufacture for it acts as a flux, (lowers the melting point). But it must be very fine-grained or else inequalities will occur in the mass. Common brick with a content of chalk and iron are comparatively easy to fuse.

Kaolin consists of extremely small crystals. If pure kaolin

is stirred up in water it settles to the bottom very slowly. The water acquires a milky appearance which can continue for months. The addition of a very little ammonium chloride causes the sinking of the kaolin particles to go on even more slowly. Common clay settles but slowly to the bottom. The presence of many salts hastens the speed of settling. Clay silt which is carried in river water thus settles out near the coast where the river runs into salt water, but not till it has passed quite a distance beyond the river's mouth if the latter is surrounded by nearly fresh water.

The use of clay for the manufacture of pottery is dependent on its plasticity in a wet condition. Le Chatelier has noted that this plasticity is due to the form of the clay particles — in fine leaflets. Coarse grained kaolin sand such as is found in Utah displays no plasticity and cannot be used at all for porcelain manufacture. On the other hand a high degree of plasticity is to be found in powders of mica moistened with water, and still more in moistened pulverized glauconite, a hydrated silicate of potassium with magnesia and iron ioxide. Both the above minerals consist of thin crystal leaflets.

In the manufacture of pottery the general processes are, after the clay has been purified by silting: the working up of the clay with water; next, the forming or moulding, then drying, then firing, and finally glazing. The amount of water kneaded-in must not be too great, or the tensile strength is lessened, and it must not be too little or the plasticity suffers. Ordinarily about 30% of water may be given as a suitable amount. If lime is present (in the form of carbonate) the amount of added water must be increased. But this is not to be desired, so, instead, sodium silicate (water-glass) is often added, and this precipitates the lime as calcium silicate. When it is a question of simpler wares such as brick, organic substances, among these a decoction of hay or straw, may be used for the same purpose. Hence the Biblical reference to "bricks without straw."

In the drying of the goods most of the water passes out and

PLATE VI

THE CULTURE-CHEMISTRY OF SILICA I. PORCELAINS.
CHINESE PORCELAIN VASE, K'ANG-HSI PERIOD
(1662–1722).

The George Walter Vincent Smith Collection,
Art Museum, Springfield, Mass.

the goods shrink. The contraction ranges between 2% and 20% depending on the amount of water and the amount of sand in the clay. This occurrence is of advantage in removing the goods from the mould. Gypsum forms a porous mould. A further contraction occurs during the burning, and depends upon the temperature of this process. According to Le Chatelier this second contraction is for clay at 800° C., 0.7%; at 1000° is 2.7%; at 1200° is 5.3%; at 1400° about 12% and at 1550° nearly 22%. This shrinkage, the nature of which is not fully understood, is in part due to the melting together of the constituents of the clay. To lessen the contraction, burned clay, or quartz sand, may be added, and these then form a sort of solid skeleton. With a volume increase of 13% quartz sand changes at high temperatures to amorphous silicic acid, tridymite or crystobalite: The shrinkage of clays can therefore be greatly reduced by adding calculated amounts of quartz sand. Indeed between 1000° and 1200° C. it is possible to obtain the opposite effect — a swelling. But the strength is lessened. In simpler products such as brick the kaolin content does not have to exceed 25%. In goods of large size however the kaolin must not be lower than 50%.

When the water passes out, air replaces it and the object thus becomes highly porous, an end to be desired for some products such as drain pipe or for porcelain filters used in bacteriology, etc. The porosity increases with the water content before burning, and increases with increased burning temperature, reaching a maximum of between 30% and 40% of the volume at about 550°, at which point the kaolin gives off its water. Above this the porosity sinks as the temperature increases, because of the shrinkage. At 1400° it is only about 5%, and in well-burnt porcelain it may not exist, whence is due the transparency of the ware. At the same time the strength and the elasticity co-efficient increase rapidly with the burning temperature above 1000° in the proportions 1:6 and 1:11 respectively between 1000° and 1200°C.

To make vessels of pottery water-tight and to give them a

beautiful appearance they are coated with a glaze. This is a true glass in which the alkalies, commonly of sodium, together with lead, tin and boric acids are the most important constituents next to the silicic acid and the alumina. The glazes are formed commonly by heating the previously baked pottery with a coating of suitable composition. Silicic acid possesses the ability to drive out other common acids such as carbonic or hydrochloric acids at high temperatures. This is partly because these latter acids are volatile at the high temperature while the silicic acid is not. The simplest way to make a glaze is so-called salt-glazing. This can be brought about by throwing common salt into the kiln during the firing. When salt-vapor mixed with some water vapor encounters the hot pottery which contains silicic acid the sodium of the salt becomes bound to the silicic acid and a soda glass is formed on the surface of the ware.

Another old process is to smear the surface of the ware with a mixture of soda or of common salt with sand stirred up in water; then, on baking, a glaze is obtained which coats the pottery. Somewhat later it was discovered that lead oxide is especially useful for glazing, so the unglazed, fired vessel may be coated with a mixture of white lead, litharge, or red lead and quartz sand, clay, or chalk, and warmed to a determined high temperature to vaporize the mixture. To obtain a white opaque glaze tin oxide may be added. This gives a milky appearance. For tin-glazed faïence-ware a lead alloy containing tin is used, four-fifths lead. This alloy is oxidized and the oxide mixture is added to an equal amount of quartz sand and one-tenth as much common salt. The mixture is then used as a glaze. The pottery which was described above as being made by burning a dough of equal parts of quartz sand, kaolin and chalk with water, is often glazed to a brown color by coating it with a mixture of one part of red lead with one-seventh this amount of manganese dioxide and four-fifths part of brick-dust. It has also been found that boric acid is useful for glazing. Such a glaze, containing 8 parts of quartz sand, 2 parts

of boric acid, and one part of lime with an equal amount of soda, is used for the glazing of a type of faïence of which the mass is made up from 45% kaolin, 45% quartz sand and 10% of potash felspar. The glaze of genuine porcelain consists of a glass containing only quartz, alumina, chalk and potash. This glass is made by mixing quartz sand, chalk, kaolin and felspar.

The chief difficulty in glazing is that the glazes may not expand equally with the baked pottery. Generally they expand to a greater degree especially at high temperatures. This inconvenience is avoided by adding the correct amount of quartz to the pottery before firing. When the ware is baked at high temperature this quartz changes to crystobalite, more and more being formed the higher the temperature. The crystobalite expands to a greater degree than the other common constituents, above 200° C. By choosing the right mixture and the right temperature of baking, the ware will expand on heating just equally to the expansion of the glaze between room temperature and the melting point of the glaze. This technique is of particular value in making the finest grade faïence. It is never possible however to obtain complete conformity. Commonly the glaze contracts on cooling more than the ware and cracks are formed in the glaze which fill with darker particles, so that the appearance of the pottery is greatly deteriorated. Such cracks also appear or are enlarged by frequent or sudden temperature changes, for instance by the use of cleaning water which is too hot. Sometimes on the other hand it happens that the ware contracts more than does the glaze when cooling. In this case a peeling off of the latter begins which is even less to be desired than the crackling.

True porcelain which has a translucent body, in order to be translucent after firing, must be heated so high that it is half melted. So that it will not lose its shape in this condition, it must be supported by moulds during firing. A high percentage of loss occurs, making the ware a costly article of luxury. Fine faïence, which like porcelain has a white background, is fired at a temperature of about 1200° C., so that its content of

quartz is largely changed to crystobalite. This produces particularly uneven expansion in heating so that the appearance is ever in danger of being spoiled from crackling of the glaze. A cheaper ware is tin-glazed faïence, which is heated to only 1000° in firing so that any considerable formation of crystobalite or shrinkage in the kiln is avoided. The ground mass is however not white but of a ruddy color, so it must be covered with a tin-oxide glaze or must be partly neutralized by adding manganese to the glaze, if translucency is desired. As a result of the slight shrinkage and the solidity of the mass no change of form is likely to occur in the firing and the loss in manufacture is slight. This form of pottery is used oftenest in daily life and has highest practical importance.

Of very great importance in our scheme of things is stoneware which in baking becomes half-melted and in this respect acts like true porcelain. It differs however by its opaqueness due to the presence of coarse quartz sand which is not dissolved during the firing. The mass is generally strongly colored by the presence of iron and manganese. The ware is given comparatively great thickness so that it does not lose its form despite its half-melted state during firing. It is often salt glazed by throwing common salt into the kiln when the temperature of the latter reaches its greatest height. When it is desired that the ware be perfectly water-tight, a glazing mass consisting of felspar with borax or chalk is used. Sometimes however the borax is replaced by a mineral found in Asia Minor called pandermite, a calcium borate.

The purer a clay is, that is to say the nearer its composition approaches that of kaolin, the higher will be its melting temperature and this for kaolin itself is as high as 1800°. Even higher is aluminum oxide (alumina), melting at about 2000° C. Bauxite is a mixture of these two bodies, kaolin and alumina. To obtain a highly fire-resistant material from clay, which is never a pure kaolin, bauxite may therefore be added, and in this way a melting temperature of 1800° can be reached. Ordinarily a fire-resistant brick may be considered of good quality

if its fusion point lies between 1650° and 1750°. By adding quartz the fusion point is lowered, yet very slowly, so that if 10 parts of quartz are added to one of kaolin the melting point is still about 1600°. With any further addition of quartz the melting temperature mounts again until it reaches that of pure quartz at about 1770° C. Of still greater power to lower the melting temperature is mica, which is a very common constituent of clays, along with lime and iron compounds. As pure quartz has a high melting point, fire-resistant quartz bricks are made and these have the advantage that they do not contract on great heating, as ordinary fire-resistant wares do when they are heated higher than their kiln temperature.

The high kiln temperature of pure clays, even when mixed with quartz, makes it desirable for ordinary purposes that clay shall not be pure, but shall be a natural mixture of various alkali silicates. Often such silicates are added to lower the fusion point. The high position of the porcelain industry of China is dependent on the addition to Chinese ware of an extremely finely powdered potash mica. Potash felspar decomposes under certain conditions into quartz and mica. Such a decomposition product occurs in China and is called *petunze*. This is added to kaolin in making Chinese porcelains. The manufacture of these porcelains was begun about 200 A.D. and reached its highest development in the Ming dynasty (1368–1644). Because of the finely powdered condition of the constituents of the mass used for Chinese procelain, it has a very high degree of plasticity, which contributes to its ease of manufacture. Other fluxes sometimes added in porcelain manufacture are mica, felspar, chalk and potassium phosphate, (sometimes as burned bone). Sometimes also iron oxide or glass are added. By the addition of such fluxes a higher density, hardness and strength can be attained in the goods.

Just as in China, the high degree of perfection of the Etruscan potteries found in abundance in Italy, was dependent upon the occurrence in that land of a clay which contained much mica and also some iron and lime. It had a particularly low

fusibility. The firing temperature was 1000° C. At 1070° it melted to a brownish glass. If the firing temperature was exceeded by only 25° a browning and darkening of the surface of the ware occurred. We must admire the extraordinary skill which the ancient potters showed in holding the firing temperature of this material at its correct height. Because of its iron content the ware had a pretty red color. It was usually decorated with paintings in black, with a paint which had the same composition as the ware itself except that there was added more alkali (about 3%), and more iron (about 7%), — in both cases about double that of the ware itself. The black color was due to the formation of a ferrous oxy-silicate. It had to be fired at a lower temperature than the baking temperature of the ware, and hastily, so that the red color of the ware could not start to darken, because of the changing of its ferric oxide content to ferrous oxide, becoming similar to the black paint of the decorations. In spite of all these difficulties the resulting products were often very thin, although the goods were sometimes of large dimensions. We cannot but admire the extraordinary skill which was displayed by the hand-workers of antiquity who prepared such delicate and artistic goods.

Of even greater importance than pottery for the development of culture, but belonging to a later historical period, is glass. Glass is characterized by its transparency which is dependent upon its amorphous nature. Sometimes glass loses its transparency and becomes turbid because of the formation of small crystals. It is then said to be *devitrified*, i.e., it has lost its property to be a glass. Glass can actually be considered as a liquid. At 1200°, for example in the glass furnace, it is indeed a liquid through which gas bubbles can rise, and which is capable of being poured into moulds. At about 1000° it is a most sluggish-flowing liquid and at about 800° it can be drawn out in threads. At yet lower temperatures the sluggishness increases till the glass can be considered as a solid body of great brittleness. Although water when it cools changes to ice which is crystalline, and this change occurs at a definite tem-

perature, glass does not show any such sharp change in cooling. Because of these fundamental differences physicists have concluded that it is a liquid. We ordinarily think of glass as transparent yet non-transparent glass is also made, such as milk-glass. This is made by adding to ordinary glass, while molten, bodies which dissolve in the glass when it is hot but crystallize out on cooling. Among such bodies are the oxides of tin and zinc, also fluor-spar and bone-ashes, (calcium phosphates). Only if the constituents of a glass do not crystallize out on cooling does the glass retain its transparency. To be sure crystals may also be transparent — for example mica (ising-glass) and quartz-crystal, and in these special cases the single-crystals are occasionally found in large enough pieces so that they might serve as "glass." Both these minerals have had some use for many thousands of years in place of glass — but never to a great extent. There are also melts of various silicates and phosphates as well as of borax which can change to a glass when they congeal. Without this more or less general property of the silicates, although very unfavorable for study by the chemist, mankind would not today have knowledge of glass. Culture, outside of sunny lands, can scarcely be imagined without window-glass. We can realize how unfortunate our fore fathers must have been when they had to content themselves with little peep-holes in the wall, closed with wooden shutters and through which at best light might be admitted by means of substances of low transparency such as horn, animal skin, thin linen or oiled paper and perhaps in a few special cases through mica sheets. Indeed more daylight came down the open chimney and shone on the hearth. The case was very different in the sunny southlands where it was rarely necessary to shut out a cold out-door air.

But glass has made great gains for science as well as for art. It has opened for the investigator the measureless celestial spheres and has opened up, too, the microscopical world that lies around us. Without glass, in other words, neither the material nor the ideal culture of today would be conceivable.

There is no question but that the art of fabricating glass arose in Egypt about 5000 years ago. Articles of glass were first brought into Greece by the mercantile and sea-going peoples such as the Phoenicians, who like the Assyrians, early learned how to work glass. The Greeks are not known to have practiced the art before the days of our calendar. Thus the Egyptians and the Phoenicians were looked upon at that time as the great masters of glass technique, and Alexandria was world-renowned for the remarkable glass articles sold in its markets.

In the Roman State glass manufacture was first taken up on a large scale in the days of the Caesars, and the products were marketed even in the far East. In China the art of glass manufacture was first learned about the middle of the fifth century A.D. In spite of the high reputation held by Roman glass it was rather highly colored, having a green or yellow tint, like the simplest kinds of glass of today, and moreover it was full of small blow-holes and nodules. On this account it was generally colored deeply or made opaque by the addition of chemicals and was used mainly for decorative purposes, and for jewelery, such as the cameo, and also for mosaics, etc. Only in very isolated cases was it used for windows; such use may be seen in the excavations at Pompeii. In the first century A.D. glass began to be used to a greater and greater extent for church-windows, but this glass was not clear, and consisted of small colored bits, which transmitted only a mystic half-light. The manufacture of glass next passed over to Constantinople and the Mohammedan Orient. The art returned to Europe during the Middle Ages. Venice became its chief center. When the Renaissance came and progress began again, glass factories, like all else, were influenced by the general desire to find artistic expression and the glass-industry of Venice reached a very high point in the 16th and 17th centuries. From Italy the art spread to France, which country was destined next to take the leading place in this branch of human culture. Even in Germany, and especially in Bohemia at the

PLATE VII

THE CULTURE-CHEMISTRY OF SILICA II. GLAZES.
CLOISONNE ENAMEL INCENSE BURNER,
CHINESE, CH'IEN-LUNG (1736–1795).

The George Walter Vincent Smith Collection,
Art Museum, Springfield, Mass.

same period a great glass industry began to develop. In the last half-century Germany has stood at the top in this field. More and more all cultural lands have attained high proficiency in the art.

The most important single property of good glass is that it will not change to a crystalline form on cooling and thus become cloudy. Among the simple silicates that of lithium cannot be obtained in the glassy condition. Even sodium silicate, when pure, easily crystallizes out, but it can be obtained as a glass by rapid cooling. The same applies to calcium silicate and to barium silicates. On the other hand it is difficult to bring about crystallization of potassium silicate or lead silicate. In mixture of substances the melting point is lowered and so too is the ability to crystallize. Thus manganese silicate or magnesium silicate each alone crystallize with ease, but a mixture containing at least 20% of both these constituents cannot crystallize. Even if it contains only 10% of one of these constituents crystallization can be brought about only with difficulty. Similar properties are to be found in the case of mixtures which contain at least 40% of potassium silicate. The addition of aluminium silicate to a mixture also hinders crystallization. All glasses in use today consist of mixtures.

The most important individual silicates are the following: Sodium silicate, (Na_2SiO_3), which may be made by heating soda (sodium carbonate) with silicic acid (quartz) to 1000°. The silicic acid drives the carbonic acid out of the soda and forms sodium silicate. This easily dissolves in water. In melted condition it will dissolve silicic acid and if this melt does not contain more than two molecules of silicic acid for each molecule of sodium silicate, even this mixture will dissolve in water. Such a solution is called *water-glass*. On concentration of this solution the silicic acid precipitates in gelatinous form. Therefore this solution is used to give strength to bandages, for the mending of glass or porcelain articles, and for the pasting on of labels which must not fall off when they are dampened, also for the preservation of eggs. In particular this solution is used

to impregnate objects to protect them from danger of fire, for example for fire-proof theatre decorations. Water-glass is also used to precipitate lime salts out of clays that are used for porcelain manufacture. Mixed with chalk or zinc oxide this silicate gives a quickly hardening cement of great strength, often used for repairing broken glass or porcelain objects.

Potassium silicate is like sodium silicate in many properties, but it is more soluble and attracts to itself more water, (is more *deliquescent*), and furthermore it is more costly, so it is not used to any great extent.

Calcium silicates are known in three different products which contain one, two or three molecules of lime, (CaO), for each molecule of silicic acid. The silicate which contains the least lime has the composition, $CaSiO_3$, and is found in nature as the mineral, wollastonite, which occurs in the type of rock known as nephelene-syenite. It also is found around volcanoes where the volcanic rocks come into contact with limestone. Another form of this silicate, pseudo-wollastonite, is to be found on the surface of blast-furnace slag.

The calcium silicate, $2CaO + SiO_2 = Ca_2SiO_4$, is found in blast-furnace slag. It falls apart into a white powder on cooling. It also is to be found in cements which have been burned at a high temperature.

The third of the silicates, $3CaO + SiO_2 = Ca_3SiO_5$, having the highest lime content, is to be found in all those cements which harden under water. Very probably, when such cements harden, the silicate decomposes into two constituents, lime and silica. The first of these takes up water forming calcium hydroxide (slaked lime), and the latter probably assumes its gelatinous form and becomes the actual bonding material which holds the cement-construction together. The hydrated lime slowly hardens by taking up carbonic acid out of the water or the air about it.

The magnesium silicate, $MgO + SiO_2 = MgSiO_3$, is to be found in nature in those very prevalent minerals which belong to the pyroxene and amphibole groups. Pyroxene also occurs in devit-

rified bottle glass. Another magnesium silicate Mg_2SiO_4 with two molecules of magnesia to one of silicic acid also is to be found in nature as a very common mineral of the peridote group. Peridote and pyroxene minerals, which both contain magnesia, often decompose in the presence of carbonic acid and water to form various products containing magnesia, silicic acid and water; the most important of resulting substances are serpentine and soap-stone. Meerschaum is also a member of this group.

The aluminium silicate, $Al_2O_3 + SiO_2$, occurs in nature as the three different minerals, andalusite, cyanite (disthene) and sillimanite. An aluminium silicate which also contains water is kaolin, made up of two molecules of silica and two of water for each molecule of alumina. When kaolin is heated to 1400° it changes to sillimanite and free silicic acid in the form of tridymite. (The water content is lost at a lower temperature,—about 500°). Sillimanite as well as silicic acid therefore are constituents of true porcelain, and also of fire-resistant brick, as well as in general of those ceramic products which are baked at high temperature.

The most important glasses are mixtures of these silicates together with more silica. According to the properties desired in a given glass the composition must be altered. The simplest glass is a solidified melt of potash felspar which consists of six molecules of silica, SiO_2, to one of alumina, Al_2O_3, and one of potassium oxide, K_2O. This glass is used for the making of glass beads. If the molecule of alumina is replaced by a molecule of lime (CaO) *Bohemian glass* ($6SiO_2$, CaO, K_2O) is obtained.

If here the molecule of K_2O is replaced by one of Na_2O then the so-called *French glass* ($6SiO_2CaO$, Na_2O) is obtained. If again in the Bohemian glass the molecule of calcium oxide is replaced by a molecule of lead oxide (PbO) one has *Crystal glass*. These, as well as mixtures made up of these, are the principal commercial varieties. Often the silica content is lowered so that only five molecules of silica enter for each molecule of alkali. A glass of low melting point is obtained in this way.

Silicic acid itself can be melted to a glass which is highly prized for its peculiar physical and chemical properties. For example threads are made from this material. These are used for the suspension of magnets in physical instruments because they lack the so-called *residual tortion*. If one twists a body hung on a metal thread or on an ordinary glass thread from its equilibrium position, and then lets it return toward that equilibrium point, it will do so only after a very long time. Such a habit is scarcely to be desired in physical instruments, and it is not displayed by quartz thread. It was the English physicist, Vernon Boys, who introduced the use of such thread in physical instruments. In the extremely sensitive string galvanometer of Einthoven the principal moving part is a silvered quartz thread. Chemical vessels manufactured out of quartz glass are not attacked by acids with the exception of hydrofluoric and phosphoric acids. Besides, this quartz has the great advantage that it can be very rapidly cooled without cracking such as would happen to a glass vessel. This is because the quartz-glass expands only slightly on heating (about 54 millionths of its volume for an increase of temperature of 100°), while ordinary glass expands nearly fifteen times as much under similar circumstances. A quartz glass vessel heated to glowing red-heat can often be dipped into water without breaking. Therefore quartz glass vessels are of the greatest usefulness in the laboratory, especially the cheaper sort, which is opaque because of air-bubbles in the quartz. Clear quartz glass is unfortunately too costly to be used except in special cases where it is necessary that light pass through unhindered. Natural quartz crystal has much greater transparency for ultra-violet light than has ordinary glass and is therefore used to a considerable extent in optical instruments.

All the above-specified types of ordinary glass are of very varying constitution. The simplest glass, *bottle-glass*, which is made from raw materials of low purity is colored due to its iron content. Green bottles contain a silicate of ferrous oxide, the red-yellow ones are colored by silicates of ferric oxide.

This sort of glass also contains quite large amounts of alumina and sometimes magnesia, commonly manganese. Window glass generally has a slightly blue-green tint from the presence of ferrous-oxide. To decolorize it manganese dioxide is sometimes added. This oxidizes the ferrous oxide to ferric oxide, which has a fainter and orange-yellow color. Such glass becomes colored gradually by the sun's rays and more rapidly by exposure to X-rays so that it acquires a beautiful violet color which comes from the manganese-oxide silicates which it contains. If one wishes one can decolorize such glass by heating it strongly, when the manganic oxide becomes reduced again to the much more faintly colored manganous oxide.

Chemical analysis shows that the window glass of medieval times corresponded most nearly in composition to the bottle glass of our times. However it contained up to double the amount of iron oxide which the bottle glass contains so it was often very highly colored. Even modern, common window glass is slightly colored.

Optical properties have played a great role in the development of glass technology. Thus glasses containing lead are noted for a high refractive power and very great color-dispersion compared with potash glasses. The former type is called *flint glass*, the latter *crown glass*. Upon this property in flint glass depends its resemblance in appearance to gemstone. Flint glass even surpasses quartz crystal in this respect and is much superior to crown glass. The beauty of flint glass may be brought out by polishing it and by facetting. If the potash in lead glass is replaced by the cheaper substance, soda, a glass is obtained which does not fully reach the beauty of ordinary crystal glass and is therefore called *half-crystal glass*. The dispersion (color-spreading) of flint glass is about double that of crown glass. Upon this fact depends the possibility of combining lenses of these different sorts of glass to attain the property known as *achromatism* in optical instruments. The lighter variety of flint glass has very nearly the composition corresponding to the formula, ($6SiO_2$,

PbO, K_2O). By increasing the content of lead at the expense of the silica heavier flint glasses may be obtained which are still more powerful in their ability to bend and disperse light rays. The heaviest and most powerful of all is pure lead silicate (22% SiO_2, 78% PbO). The refractive power of lead glass can be increased by adding bismuth and by replacing the potassium by the element thallium, which has properties very like those of lead. Such a glass however has various properties less to be desired such as that it is easily scratched and easily attacked chemically. For the preparation of counterfeit precious stones a glass is used which is called *strass*, (also *paste*) and which has a high content of lead but contains comparatively little silicic acid. Its hardness is therefore much lower than that of true gem stones, and it can be easily scratched and rapidly loses its glance.

When the great reformer in the field of optical instruments, Ernst Abbe of Jena, calculated how best he could accomplish his desires, he soon found that if a glass could be made that had certain desired properties he could carry out his endeavors. He sought to produce lenses which would give images completely free from color distortion, further to find glasses which had high refractive power but a low color dispersion and vice-versa. At that time there actually were known but two sorts of optically different glass, crown glass which had no lead, and flint glass of a high lead content — together with certain intermediate combinations. This was entirely too little material for proper construction of instruments. "In a year," said Abbe, speaking for himself and his co-worker, Carl Zeiss, "we have drifted, so to speak, into imaginary rather than true optics. We have taken into account the construction of lenses in which a hypothetical glass is used, one that is actually not known at all and we have debated upon the progress which would be possible if simultaneously all the glass factories should turn their attention to the higher problems of optics." They carried out researches upon liquids which possesssed the desired properties, and such researches began particularly well,

PLATE VIII

THE CULTURE-CHEMISTRY OF SILICA III. GLASS.
VENETIAN GLASS, 16TH–19TH CENTURIES.

The George Walter Vincent Smith Collection,
Art Museum, Springfield, Mass.

This series of illustrations of objects of art will serve to remind us that beneath æsthetic culture, there is a material culture, a chemistry of metal or pottery or glass, which makes possible the higher culture.

but for obvious reasons were impractical. After some time there appeared a young doctor — Otto Schott, who had read Abbe's opinions on this question and offered to collaborate. He first made glass melts on a small scale, between 20 and 160 gms., out of combinations of all sorts of substances which could possibly form a glassy material. These products were examined with the aid of the spectroscope to determine their optical properties. Finally this young man succeeded in enlisting the support of the Prussian ministry of education. In this way there was founded in 1884 the famous Schott glass laboratory, which succeeded after a few years in preparing a great number of new sorts of glass, some of which had the properties required by Abbe. Thus it became possible to perfect to a high degree the technique of the microscope and the preparation of all sorts of optical instruments. But they were not content with even so fine a result as this. By trial, types of glass were found which had desirable properties of heat-resistance, so that they were suited for example to the manufacture of thermometers, which must have as little likelihood as possible of change of the zero-point in use. They then prepared alkali-free glasses which could be used by the chemist for the keeping of acid solutions without contamination of these solutions by alkali from the glass. They made a glass that did not dissolve in water to any noticeable degree so that distilled water of the highest purity could be kept in vessels of this glass, where before expensive platinum vessels had been necessary. Such glass is used also to measure the height of water in boilers, and does not corrode or break. They prepared types of glass which are used for the insulation of electric wires. Such glasses are completely non-conducting until the moisture content of the air about them exceeds 80% saturation. These glasses are, as one may imagine, closely related to the alkali-free glass used in chemical work. By introducing into a glass only elements of light atomic weight a material can be made which only slightly absorbs X rays. Types of glasses can be made of various desired mechanical property such as elasticity, hardness and

difficult breakability. This latter property is of importance for instance in the construction of mercury thermometers, which are used for temperatures up to 450° — nearly 100° above the boiling point of the mercury so that they must be able to withstand very high pressure.

Schott's enterprise succeeded so well that financially also it was self-supporting. When the war broke out and severed the communications between peoples, it became impossible to procure in the countries which were fighting Germany, and also in neutral lands, glasses manufactured by the famous German factories, that previously had completely commanded this important field. To relieve the embarrassing shortages in all these lands and particularly in England and America great glass works were built whose purpose was to replace the unavailable German goods. These enterprises were remarkably successful, and brought forth new and better types of glass. The isolation caused by the war taught various new lessons.

Among these "Pyrex," an American glass developed by the Corning Glass Co., has come into use not only for chemical glassware but to replace baking dishes in the household, for baking pastries and bread in the oven. It surpasses the German glasses in its ability to withstand changes of temperature. Baking dishes can be made quite thick and thus possess great mechanical strength. Its composition is:

Silica	80.5%
Boric acid	11.8
Alumina	2
Sodium oxide	4.4
Potassium	0.2
Calcium oxide	0.29
Iron oxide	0.25
	99.44

Another American product is "Precision Glass," made by the Kimble Glass Co., and used for the preparation of calibrated laboratory apparatus of precision. The Geophysical Laboratory in Washington has furnished great aid to the

glass manufacturer by developing a diagram from which the physical constants of a glass can be predicted.

Although color and opaqueness in a glass is usually to be considered as quite a defect, colored opaque glasses have been made for artistic purposes such as stained glass windows. The commonest coloring materials for glass are: cobalt to give a blue color, iron for blue-green or red-yellow, gold for purple-red, copper with iron and tin for blood-red or for blue-green, chromium for green or for rose-colored, manganese for violet, titanium to give bluish red or yellow. Glass which has lain for a long time in the earth shows an irridescent surface. This is due to the partial solution of the glass. The same effect can be obtained by boiling the glass with dilute hydrochloric acid for some hour's time. Irridescent colors also result from the solvent action of water upon old window panes.

From lime-glass which is long heated to a high temperature there separates long crystals of pseudo-wallastonite (Ca silicate). As a result the glass acquires a porcelain-like appearance. Such glass is named after Reamur who first noted the property. Attempts have been made to use this glass as porcelain but it is found to be very brittle so that it has little use. Zinc oxides can be dissolved in glass to such an amount that on cooling it crystallizes out in long needles. These can be colored a green or blue color by adding nickel or cobalt, which enter into the zinc silicate crystals. This fact is made use of for the preparation of artistic glazes on porcelain. Aventurine glass is characterized by the presence of small red copper crystals embedded in the glass. It results from the presence in the glass of both copper silicate and ferrous oxide. The latter during a slow cooling of the glass is oxidized at the expense of the copper oxide out of the silicate, so that copper precipitates in crystalline form.

It has been stated above that calcium silicate is an essential constituent of cement. The Romans used a volcanic rock called *pozzuolana*, very much like pumice stone, for the building of their famous aqueducts. A famous civil engineer, John

Smeaton, was commissioned by the British Parliament to erect lighthouses on some skerries in the English channel that were very heavily swept by wind and wave. Previously attempts had been made to use wooden edifices but they had been rapidly destroyed. Smeaton sought for a material which after burning and wetting would harden under water, in contrast to ordinary wall-mortar which will not so harden. He found in Cornwall a clayey limestone that possessed this property. By mixing his "hydraulic lime" with pozzuolana, Smeaton obtained in 1756 a cement from which the famous lighthouse at Eddystone, England, was then constructed. This cement was called Roman cement. But the pozzuolana was expensive and types of limestone were sought for which would on burning give directly a cement without further additions. Various such deposits were found and numerous patents were taken out on methods of preparing cements. The most important of these was obtained by a mason named Aspden in Leeds in 1824. He called his cement Portland cement for he noticed that after hardening it resembled a much sought-after building material known as Portland stone. The raw materials for the new cement was a mixture of silica rich clay with limestone, and it was then burned in a lime-kiln. It was soon found that the temperature of firing thus obtained was too low. The heat ought to be great enough, it was found, so that a partial melting together of the material would take place. We know today that such a temperature is necessary in order that tri-calcium silicate may form. The early workers made investigations of various mixtures and kiln temperatures and so gradually bettered their product. Portland cement is far superior to other cements, so that it has become a widespread notion that a better cement cannot possibly be obtained. Such progress as has since been made has mainly been concerned with the mechanical handling, which brings about an intimate mixing of the constituents by means of a powerful milling of these to form a fine meal. The constituents commonly are lime, alumina, and silica, also some iron and magnesia, which are not with-

out desirable effect. All these components except the lime are to be found either in clay or in furnace slag. So these substances, together with limestone, make up the principal raw materials. England was the first principal producer of cement, next Germany, and now the U. S. According to Mead the composition of the best American Portland cement is:

Lime, (CaO)	63.5
Alumina, Al_2O_3	7.5
Silica, SiO_2	22.5
Iron Oxide, Fe_2O_3	2.5
Magnesia, MgO	2.5
Sulfates — (K_2SO_4 or Na_2SO_4)	1.5

The three last named constituents are not absolutely necessary but they lower the firing temperature by not less than 225°, from 1650° to 1425° C. and this brings about a great saving of fuel, so that any decrease of strength due to the impurities is more than balanced economically. These impurities are what gives cement a gray-green color. If they are absent its color is a pure white.

Cement has been investigated by many research workers. The most important results have been obtained by the great institutions in America — the Bureau of Standards and the Geophysical Laboratory of the Carnegie Institute, both in Washington. Analyses made by the latter institution of the constitution of the burned material (clinker) show about 45% tricalcium silicate, 35% dicalcium silicate and 20% of tricalcium aluminate. This is in a cement free from impurities.

In America cement is made from clays of high silica content. These are fine-ground. The limestone is prepared similarly. Both materials are then mixed and ground in ball-mills, an analysis of the mass is made and the constitution finally adjusted. The mass is then conveyed to the upper end of a steeply inclined tube of sheet steel, lined with fire resistent brick. The dimensions of the tube are 18–45 meters in length and 15–25 meters in diameter. It is set into gentle rotational motion by means of cog-wheels and it is supported on friction

rollers. The material slowly passes down the tube to the lower end, (time about $1\frac{1}{2}$ hour). This lower end is heated to the kiln-temperature, ordinarily about 1425° C., by means of the blowing in of finely-powdered dried coal-dust with compressed air. The heat drives the combustion gases out of the upper end of the tube and they give their heat (in passing) to the slowly sinking mass. The process can be described by the following data (according to Rankin):

1. Raw materials: { Limestone, $CaCO_3$ / Wet clay containing silica: { Al_2O_3 / SiO_2 / H_2O
2. at 1000°: { Lime, CaO / Alumina, Al_2O_3 / Silica, SiO_2
3. from 1000° to 1335°: CaO, $(5CaO, 3Al_2O)_3$, $(2CaO, SiO_2)$, $(3CaO, Al_2O_3)$.
4. from 1335° to 1450°: CaO, $(3CaO, Al_2O_3)$, $(2CaO, SiO_2)$, $(3CaO, SiO_2)$, Melt.
5. from 1450° to 1600°: CaO, $(2CaO, SiO_2)$, $(3CaO, SiO_2)$, Melt.
6. The cold clinker: $(2CaO, SiO_2)$, $(2CaO, SiO_2)$, $(3CaO, Al_2O_3)$.

Cement burned from impure clay (note Mead's analysis above), contains about 36% tricalcium silicate, 33% dicalcium silicate and 21% tricalcium aluminate with 10% of other constituents. It often happens however that the kiln temperature is not correct. In such an event, if too low, only a small amount of the most desirable constituent, the tricalcium silicate is formed. Sometimes also free lime is left. This is injurious if it occurs in large amount, for a building made of such cement will crack, due to the taking up of water by the lime and the resulting swelling. When the clinker is made it is then fine-ground, and the cement is ready to use.

Cement mixed with water forms a solid mass after a time. The change from the plastic to the solid state is called setting, and takes several hours. Then there follows a slow hardening which occasionally extends over a year's time. Dicalcium silicate sets very slowly and this is why it is held to be of comparatively low value. Tri-calcium aluminate sets and hardens rapidly but it is slightly soluble in water so it is not especially

strong and tenacious. Tricalcium silicate sets and hardens somewhat more slowly than the aluminate. However it is the only one of the three constituents of cement which can alone give a solid mass, with strength and solidarity comparable with those of the mixture, the Portland cement. The binding and hardening materials which form from the tricalcium silicate and the tricalcium aluminate consist of amorphous gelatinous masses, probably gelatinous silicic acid and gelatinous alumina. Of these the former undoubtedly has the higher bonding properties. A bonding action due to gelatinous silicic acid takes place in nature in the formation of sand-stone out of grains of quartz sand which became cemented together by amorphous silicic acid.

Cement has been used in very great quantities in the last few decades for the preparation of concrete for building purposes. In the U. S. alone in 1920, 97,000,000 barrels were used, corresponding to 16,000,000 tons with a value of about 194,000,000 dollars. The amount used in the forty years previous to that date was by comparison insignificant. Concrete construction dominates more and more in the architecture of great edifices.

Many researches have recently been made to attempt to prepare potash from silicates containing this substance, such for example as potash mica, but especially from potash felspar. If one part of a potash felspar is heated with three parts of limestone for one hour at 1300° to 1400° the potash will be volatilized for the mass and can be condensed on cooling as a fine ash, while the remaining clinker can be ground up and used in a Portland cement. By adding calcium chloride the process can be accelerated and this result can probably also be brought about by other fluxes.

The clays used in cement manufacture generally contain some potash and if the temperature of the kiln goes above 1400°C. it is to be expected that the potash will in part volatilize out and pass off as dust in the flue gases. It has been found in America that this is so, and now the flue dust and the

escaping potash are saved. Yet the time during which the particular material in question is heated above 1300° is so short that the reaction cannot become complete — so only a small portion of the total potash is thus made available.

The chemist, William Ross, at the University of Washington in Seattle, has investigated a process which appears to be most promising: He first tried to get potash from potash felspar by heating the rock with steam at 500°C. and under the enormous pressure of 1450 atmostphere. This experiment was unsuccessful. Next he heated the felspar with lime in water at 300° under about 90 atmospheres of steam pressure. He then found that a large part of the potash had been displaced by the lime, and had dissolved in the water. When the lime was made double the amount of the felspar, practically all the potash was freed. He now added still more lime so that the mass remaining after leaching out the potash would have about the same composition as the mixture from which Portland cement is made. (Felspar is about 25% low in alumina in comparison with the silica content, but this seems to make little difference in the value of the product). He investigated the potash yield at different temperatures. It was found that at 200° and 16 atmospheres pressure, 93% of the potash could be separated. At higher temperatures higher yields were possible, but it was convenient and more practical to work at the low temperature of 200°. So it should be comparatively simple to design an economically advantageous process along these lines, first removing the potash, then making cement from the remaining mass.

Chapter VI

THE CHEMISTRY OF THE EARTH'S CRUST

Since we have just been considering the most important minerals of which the solid earth's crust is composed, quartz and the silicates, we might turn our attention to the changes which that crust undergoes with lapse of time.

The specific gravity of the whole earth has been determined by many investigators and has been found to be 5.52. This is remarkable because the rocks making up the solid crust of the earth have a mean specific gravity of only 2.6. The only explanation is that the inner portion of the earth, approaching the center, must have a considerably higher specific gravity than 5.6. Long ago it was concluded that the nucleus of the earth consisted mainly of iron, whose specific gravity is 7.9. Chladni proposed this in 1794 on the basis that the meteorites are mainly iron, and because of the magnetism of the earth. Later it was determined with the spectroscope that iron is probably the most important constituent of the sun. In the crust of the earth, iron is next most important to aluminium as a metallic constituent. We must conclude that the center of the earth consists of metals, very probably molten and that iron is probably the chief component. This central mass makes up something more than half of the whole earth-mass. Over it there lies a lighter mass whose composition seems to correspond to that of igneous rock. In the deeper layers of this material prevails rock containing the heavier iron, magnesium and aluminium silicates. Higher up come lighter silicates in which the iron and magnesium are replaced by the lighter metals, calcium, potassium and sodium, and uppermost lie layers richest in silica, (quartz), which is the lightest of such

rocks. Very probably all these silicates, save the uppermost, are in molten condition. This molten material corresponds to the magmas thrown out by volcanoes.

By the analysis of material from volcanoes we can gain an idea of the composition of such masses. Among the substances contained are gases which pass off into the atmosphere. These are of interest because they have contributed to the formation of the atmosphere. Many researches on the composition of such gases have been made. Among the oldest of these were analyses made by the famous chemist, Bunsen (1811–1899) who made investigations of volcanic exhalations during a trip to Iceland. Besides the ordinary gases of the atmosphere, he found them to contain sulfur dioxide, carbonic acid, hydrogen sulfide and hydrogen gas. The three latter were in largest amount. The bulk of the material was water vapor. A French chemist, Brun, opposed the idea that gases brought forth by volcanic action direct from the interior of the earth have any water content. He claimed that the water observed over volcanoes, which often condenses during eruptions to a heavy rain darkened with volcanic ash, was water which had flowed in as rain or ground water. But the researches of Day and Sheperd on the gases from the crater of Kilauea in the Hawaiian Islands have demonstrated that this could not be the case and that the water actually comes chiefly from the magma. The water contains various mineral salts, such as fluorides, chlorides and sulfurous acid. Also vapors such as hydrogen chloride are quite commonly present in the volcanic gases. It is claimed that this latter constituent results from the action of water on metallic chlorides, which are changed to oxides. With the decline of active eruption the strongly acid gases, hydrogen chloride and sulfur dioxide are replaced by hydrogen sulfide and carbon dioxide, while water vapor continues to be emitted. Carbon dioxide streams from the fumaroles and springs in districts of diminished volcanic activity, for instance in the Eifel region in Germany. Ordinarily volcanic activity ends when only water, as vapor or liquid, streams forth. The hydro-

gen which passes out from active volcanoes may catch fire on issuing into the air, as it does at Kilauea. If the volcanic activity decreases and the temperature drops, the hydrogen may pass off without burning. Marsh gas is also to be found in many volcanic gases. This doubtless burns as does the hydrogen when it reaches the air, should the temperature be high enough. Chlorides are also found in the hot gases, fluorides occasionally, and sulfates of heavy metals, especially of iron and copper, — furthermore, ammonium chloride and sodium salts and a few potassium salts. Boron salts often are present. In many cases free sulfur deposits itself around the orifices whence the gases issue, as in Sicily. This sulfur results from the action of sulfur dioxide on hydrogen sulfide, which oxidizes the latter and reduces the former.

Many rocks such as granites are buried under the surface of the earth and cannot therefore have given off their gas-content to the air. The gases are still locked up in the stone. If the stone is crushed and pulverized and the powder heated the gases pass out. So much gas is occasionally present that the stone explodes when it is struck by a hammer. This is true of the red quartz from Branchville, Conn. Similarly granite from Monson, Mass., is let stand some time after quarrying, and little particles of stone often fly at high velocity from its surface as the gas pressure is relieved. The gas content of the Branchville rock is made up of 98% carbon dioxide, the rest nitrogen with a trace of other gases. Granites and gneiss give off gas amounting to $2\frac{1}{2}$ to 7 times and even up to 18 times their own volume, measured at 18° C. and atmospheric pressure. These gases are mainly hydrogen and carbon dioxide with a little methane, carbon monoxide, nitrogen and hydrogen sulfide. Water is not generally present, though at times it may be the chief constituent. Gautier calculated that a cubic centimeter of a granite which he investigated when heated to 1000° C. gave off 20 liters of gases, and 89 liters of water measured at 1000° and atmospheric pressure. Very often the vapors from volcanoes attack rock masses lying nearby,

setting free carbon dioxide from the limestone, and hydrogen sulfide from sulfur compounds.

The temperature of liquid lava is quite high. Day measured it at Kilauea and found that it was 1000° C. in the uppermost layers; deeper down it was still higher, as may be concluded from the minerals which crystallize from lavas, whose melting points lie between 1100° and 1500°.

The solidified magma constitutes the so-called *igneous* rock; if formed at great depth, called plutonic, if nearer the earth's surface, intrusive, and if poured out on the surface, volcanic rock. The latter differs in that its magma gives off gases. The rock which forms may be crystalline or glassy according to the conditions prevailing during cooling, and especially depending on the speed of cooling. Between the two extremes, wholly crystalline and wholly glassy, there are many intermediate conditions. In crystalline rock the minerals of which it is composed can be determined, and their proportion to one another. Clarke gives the following table for the average composition: Felspars 59.5%, hornblende and pyroxene 16.8%, quartz 12.0% mica 3.8%. The remaining 7.9% consists of a number of minerals present in small amount. Felspar is the main constituent, next comes the iron and magnesium silicates, and third the pure quartz.

If these rocks come into contact with air and water, changes occur, both mechanical and chemical. The following are factors in the mechanical decomposition of rock: Glaciers plane off the rocks they pass over with the aid of cobble-stones and grit which they carry embedded in them. Of stones thus formed from rocks, the larger masses also become embedded in the glacier, the fine particles are carried away by the melt-water, and this latter thus becomes milky in appearance. The waves along the shore of lakes and oceans similarly break up and grind the cliffs along the shore, and streaming water everywhere erodes rock. Water seeping into cracks freezes in cold weather, widening the cracks and so prying off both large and small pieces of the rock. Sand driven by the wind against the

face of a cliff acts like a sand-blast, so that with time the rock crumbles away. This latter mechanism is especially active in desert regions where no covering of plants binds the sand. Growing plants located on rock surfaces, drive their roots into the cracks and crevices and so enlarge them.

Mechanical action, however, is not as erosive as chemical action. In a sense one can look upon the mechanical decomposition as a preparation for the chemical action, since it provides greater surface for attack. The chemical erosion is largely caused by water and by substances dissolved in the water. Water takes up oxygen and carbon dioxide from the air. While the atmosphere contains 21% of oxygen and only 0.03% of carbon dioxide, the gases taken up by rain water at 0° contain nearer to 34% oxygen and 3% carbon dioxide. At 25° the oxygen is above 34% while the carbon dioxide has sunk to about 2%. When rain water sinks into the soil these gases are given up, and this so completely that according to B. Lepsius at 25 meters depth the oxygen content of the ground-water is scarcely one-third of that held at the surface. Carbon dioxide is taken up by the soil, but is again carried away by the ground-water, so it cannot be determined how much of this gas the rain water gives up. The oxygen carried down into the soil forms acids from the organic matter — humic and carbonic acids. An important process is the oxidation of iron sulfide, (pyrite), forming iron oxy-sulfate, which decomposes into free sulfuric acid and iron oxide. The sulfuric acid attacks the minerals of the soil and changes them into sulfates.

There is scarcely a silicate that is not soluble to some extent in water. Such solutions precipitate silicic acid and form a hydrate with an alkaline reaction. It has long been known that many minerals when moistened with water give an alkaline reaction to test papers, such as the litmus paper much used by the chemist. Their solubility in water is greatly increased by the presence of carbonic acid. The carbon dioxide combines with the free bases to form acid carbonates which are quite soluble in water. Many investigations have been made to de-

termine the solubility of different minerals in both pure and carbonated water. In 1848, S. B. and R. E. Rogers found that pulverized hornblende after 48 hours treatment with carbonated water was dissolved to the extent of 1%. Similar researches by R. Müller (1877) showed that powdered potash felspar after treatment for seven weeks with carbonated water had given off one and one-third percent of its content of potash, but only 0.14% of the alumina and 0.155% of its silica. It is clear that this process could go on until felspar, made up of alumina, silica and potash, could be changed in part to a product containing only alumina and silica, together with some water. This product exists in nature and is what we know as kaolin. From other felspars there result bauxite and laterite, in which even the silica has separated from the alumina so that only aluminium hydrate with a little iron oxyhydrate remains. This latter constituent, the iron, gives a strong red coloration to the laterite, which is quite a common mineral in the tropics. Bauxite is a commercially important mineral, for it is the raw chemical for the preparaton of aluminium metal. The substances that are most completely removed from the silicates by water are generally lime, magnesia and iron oxide (according to Müller). These dissolve in the water in the form of acid carbonates and are carried away to be precipitated elsewhere when they come to lose part of their carbon dioxide. Thus they form new layers of limestones, or dolomites, and of limonite, (or bog iron ore). Such experiments in solubility have been made upon oligoclase, hornblende, olivene and serpentine. An experiment with powdered apatite has proven that a considerable amount of phosphoric acid (up to 2%) as well as lime goes into solution. From magnetite, an iron oxide, carbonated water removes between 1 and 2.5% of the iron oxide. All the above figures are for a test period of seven weeks action of carbonated water upon the powdered rock.

Thus rain water with its carbon dioxide dissolves many things, lime, magnesia, alkalies and iron oxide, in the form of

carbonic acid salts, and carries them from their original resting place. The iron oxide precipitates as limonite, which may be carried further by water currents. The rock that remains after these things are leached out takes up water, and so felspars are changed to quartz and kaolin, or to quartz and bauxite or laterite. The magnesia minerals change over to talc and serpentine. Much of the quartz remains as quartz sand. Water saturated with mineral matter and seeping through the soil often carries organic substances from the decay of living matter. These have a reducing action and so iron sulfate may be changed into iron sulfide. Humic acid forms hard masses with iron oxide; often impenetrable layers are so formed. Alkali dissolved in the seeping water may bring about increased solution of the silicic acid, then this dissolved silica may cement together sand grains, so that new stone is again formed to replace the weathering of stone, a process which is continually going on over the surface of the earth.

Rivers not only carry substances dissolved in their waters but they also carry considerable solid matter. The largest of such particles, stones and gravel, settle to the bottom onto the stream bed. These, like the sand carried along by the river, consist of pieces of the native rock, but sand has a preponderating amount of the quartz of the rock. The solid matter is partly washed along and partly is to be found in hydrated condition as a fine silt; this latter is principally made up of kaolin (hydrated alumina) and iron oxide. The silt formed by the grinding action of the under-surface of a glacier corresponds to the original rock in its composition; it has not been acted upon chemically. The glacier ice and the freezing temperature have protected the material from the action of oxygen and carbon dioxide. Clay formed from this material therefore contains more soluble matter such as lime than does that formed by ordinary weathering. The same is true of loess, an aeolian formation, (that is to say, a product formed in a dry way by the erosive action of the wind). Loess is distinguishable by the sharp edges of its particles, in opposition to the rounded

condition of particles which have been rolled along by water. Also loess is characterized by a high porosity, due to the shape of the particles. At last the dissolved substances and the finest of the silt pass into the sea. The silt precipitates near the shore though it may be carried about for some time by the currents, as it is for example before the mouth of the great Chinese rivers, in the Yellow Sea, and before the mouth of the Amazon in the Atlantic. Settling of the silt is speeded by the salt content of the sea water. There also collect on the bottom of the ocean great quantities of volcanic ash, and that material which is carried by icebergs away from the land. The continuous precipitation everywhere of cosmic dust in the course of time contributes to the mud of the sea bottom. Salts of calcium and magnesium, and silicates which are carried out to sea in solution are taken up by organisms, and the shells and skeletons of these are continually sinking and building deposits on the floor of the sea. Such layers lie for the most part near to the shore, and here the remains of coral animals and shell animals are often ground by the waves into a sand. At great depths there are silica deposits which are formed from the remains of diatoms and radiolarians, and there are lime silts, arising from the remains of globigerina and pteropods. All these organisms actually live in the upper water layers and their remains sink after death to the sea bottom. The greater portion of the bottom of the sea is covered by a red mud, 60% silica, 16% alumina and 10% iron oxide, with water, magnesium, calcium and sodium, in small amount. This is a composition very like that of the igneous rock, diabase. The famous oceanographer, Sir John Murray, came to the conclusion that these red sea-muds originated from volcanic eruptions.

The weathering and the decomposition of igneous rocks, as just described, is of great importance in the continuation of life on earth, for it is the process by which loose surface layers have formed. These consist principally of sandy and limey soils and there are all degrees of mixture of these two types. In these soils are found much undecomposed mineral, as well as lime

and magnesia, things which are needed by the plants, and therefore also for animal life. From these loose soil-layers rock may again be formed by the influence of high pressures, high temperatures, or by the introduction of cementing material. In this way sandstone forms from sand, shale from clay, limestone from chalk or chalk sands. Between these extremes there are all possible gradations.

For a sand to become a sandstone a cementing material must lie between the grains. Spherical sand-grains all of a common size, close packed, have a free space of 26% of the total volume. In the case of uneven grains the free room is still greater, if still finer particles do not happen partly to fill the intermediary spaces. Actually this is not often the case. Moving water sorts the grains and lays those of about the same size together. So water can find quite a playroom in sand. Such water will often contain considerable dissolved or silted material and this can be deposited between the grains and bind them together. Dissolved silica or calcium carbonate or other lime salts, sulfates, phosphates, fluorides or the gelatinous hydrates of iron or aluminium, and even clays and bituminous bodies, may make up this cementing material. In most cases the quantity of infiltered material is less than the sand, but may occasionally be greater in amount than the sand. Depending on how much of the space between the grains becomes filled by these substances, a more or less compact sandstone will form. Sandstones are known which are flexible in not-too-thick masses. Sometimes the cementing substance crystallizes and the sand grains become enclosed in these crystals. At Fontainebleau there is a crystalline limestone with an enclosure of between 50 and 95% sand. Naturally the composition of a sandstone depends in part on the sort of sand from which it originated, which may be pure quartz, or mixed with felspar or mica, and also of course it depends on the nature of the cementing material.

Masses cemented together from large cobblestones or pebbles are called *conglomerate*, *puddingstone* or *breccia*. A noteworthy

form is *flint*, which has played its great role in our cultural past. Such a quartz silt as is found on the sea bottom might become hardened by the infiltration of dissolved silica, which could crystallize out between the skeletons of the diatoms and radiolarians. For flint is not amorphous as is often claimed, but is micro-crystalline. It is often claimed that flints have altered from old lime formations, and that the lime has gradually dissolved away and been replaced by silica. Such metamorphoses are known at Tampa, Florida. The case is like that of the petrified forests of Egypt and Arizona, where silica solutions have penetrated the woody trunks and replaced the organic matter. In many flints one finds the deposition of quartz on the quartz spines of sea-sponges. Most flint balls which are found in chalk layers and in which the quartz lies here and there in a chalk network between the original quartz needles, seem to have formed in this manner.

If a finely divided material containing considerable alumina becomes subjected to a high pressure a leafy mass called *shale* is formed. In this case a binding material is not necessary though it may be present. According to the view of Le Chatelier the plasticity of clay depends on the fine-plate-like form of its particles. Probably capillary attraction holds these particles together and prevents water from passing between them and separating them. By the action of high pressures the contacts between the particles become greater and a welding together results. The water is pressed out and a clay-shale results. High temperatures favor the change, and cause many minerals such as chlorite, mica and various carbonates to crystallize out.

Limestone is almost entirely formed by the action of organisms. Calcium carbonate can be thrown out of water containing dissolved calcium bicarbonate if the carbon dioxide escapes. Such a precipitation occurs in the formation of stalactites, stalagmites and drip-stones in caverns in lime-stone regions and in the lime-sinter, or tuffa around springs, especially hot springs. Similar precipitates form in the sea, but are of

slight importance. Generally, and principally, lime is deposited by organisms.

On the coral reefs the different stages of limestone formation are evident. Beside the living coral animals, lie dead sections, which become ground by the waves to a coral sand. Nearby one can see how this sand becomes bound together by the crystallization of calcium carbonate at the points of contact of the grains, when the sand lies undisturbed by the waves. Finally a solid rock results, in which one can still see remains of the original coral. Many useful studies in the field have been made by Spring and he has found that solid bodies can be made by pressing together powders. He subjected dry pulverized limestone to a pressure of 6000 to 7000 atmospheres and obtained, after seventeen years, a hard block similar to crystalline limestone. Doubtless the process would occur still faster if the powder were moist.

Limestone is one of the most useful raw materials of chemical industry, a well as in the building trade. When heated, it loses its carbon dioxide. At a little above 900° C. (1650° F.) the pressure of the carbon dioxide given off reaches one atmosphere. At this temperature one can therefore say that that carbon dioxide *boils* off just as does water when its vapor pressure becomes greater than that of the atmosphere. In this process limestone changes into "burnt lime," calcium oxide, CaO. If this latter is mixed with water it forms "slaked lime" and there is a great evolution of heat. The latter substance is a fairly strong alkali. Limestone is to be found widely distributed in nature. One can burn lime and make slaked lime, and use this to set free alkalies from other salts on a technical scale. In this way the most important of the bases, potash and soda lye were formerly made. Their carbonates were boiled with slaked lime. (Electrolytic processes are used at present.) Ammonia is prepared by heating ammonium chloride with slaked lime.

The boiling point of the carbon dioxide from lime increases with increasing pressure just as does the boiling point of water.

Boeke forced the boiling point from limestone so high that the stone's melting point was reached, and was found to be 1289° C. (2354° F.) at a carbon dioxide pressure of 110 atmospheres. Boeke also succeeded in melting the carbonates of barium and strontium, which are closely related to limestone. These carbonates occur in nature as witherite and strontianite. The melting points are 1600° and 1470° C. at 90 and 60 atmospheres of carbon dioxide pressure respectively.

The flakes of lime that are precipitated by organisms contain a little magnesium, and on the average this amount is 1%. Many algae remove even more magnesium carbonate, in some cases up to 13% (according to Högbom). From such material magnesia-limestones are formed. Högbom has further shown that when such rock is weathered by carbonated water, lime dissolves out faster than does magnesium and so the residue approaches nearer and nearer in composition to dolomite, $MgCa(CO_3)_2$. Also water containing magnesium salts in solution can wash calcium carbonate out of limestones and replace it with magnesium carbonate. Dolomite, and dolomite limestones are widely distributed rock material.

These rocks often contain iron, partly due to the action of plants, which may cause iron carbonate to be precipitated along with the lime and magnesia. Iron carbonate can replace calcium carbonate just as can the magnesium salt when solutions containing iron come into contact with limestones. In this way large areas of iron-spar or siderite (iron carbonate) are formed. In the presence of water containing oxygen this mineral easily changes to limonite (iron hydrate) and this, by the action of heat and pressure, to hematite, Fe_2O_3, or to magnetite, Fe_3O_4. The remarkable, huge, iron deposits around Lake Superior are believed to have been formed in this way from original deposits of siderite.

Heat and pressure are the agents which have produced the greatest changes in the original earth deposits. The so-called crystalline shists, the more important of which are the gneisses, mica shist, chlorite shist, talc shist and marble, were long a

difficult problem for the geologist seeking to learn their origin. On the one hand they had the same layered structure as the sedimentary deposits which must have been laid down under water. On the other hand they could be seen to be crystalline, like rock of igneous origin such as granite. All possible intermediary states between granite and gneiss may be found, and between mica shist and sedimentary clay-shales. The Norwegian geologist, Reusch, found crystalline shists near Bergen, Norway, which contained fossils, petrified organisms, which made it appear certain that these shists must originally have been laid down under water. Such fossils are also to be found in the well known marble deposits of Carara.

Thus these rocks must have changed from sedimentary deposits to crystalline shists. Such a change would take place at high temperatures and these temperatures may have arisen in various ways. Magma may have intruded into the sedimentary layers and thus these layers may have been highly heated, then slowly cooled. Or the original layers may have become covered with great thicknesses of new deposits, or might by dropping or folding have been carried down to a great depth below the surface. The temperature below the surface of the earth increases about 30° for each kilometer (about five-eighths of a mile). In such layers, if they lay a few dozen kilometers below the surface, the temperature could reach a point where crystal formation might result, or the mechanical action of faulting or folding might produce the necessary heat. This heat frees the minerals of their water content, which they may have when near the surface. The remains of organisms, containing carbon, char and become graphite.

A question of great interest, that of how long the earth, undoubtedly originally gaseous, has taken to reach the condition of a solid crust partly covered by ocean has been answered in recent years with great accuracy. It was customary among geologists at the beginning of this century to allow a period of 100 million years for this. The most probable of calculated values was considered to be that of Joly — 95 million years —

the time necessary for the sea to have gained its present salt content by the contribution of rivers. However geologists soon came to the conclusion that a much longer time — 1000 million years, must have passed since organic life first arose on earth. All available calculations were equally uncertain.

But the discovery of the radioactive minerals and of the phenomenon of radioactivity produced a change in this situation. If a radium preparation is preserved in a glass vessel this glass becomes colored a dark violet color. When the glass is heated the color disappears. This coloration results from the action of the radiation from the radium, and it develops more rapidly the more rays the preparation sends out. It has been known for a long time that many minerals such as tourmaline and mica display under the microscope dark spots in their layers, which are called "pleochroic halos," (places which under polarized light show various colors). Joly in 1907 discovered that these dark places were due to radiations from little, enclosed kernels of radioactive material, containing uranium. From measurements of the size and the uranium content as well as by intensity of the color of these spots, it was determined that these preparations which came from a rock of the Devonian period had an age of about 400 million years.

The radioactive substances give off helium and slowly change to lead. This change takes place extremely slowly. A ton of uranium would give at the end of one year 0.11 cc. of helium and 0.13 milligrams of lead. There are a number of minerals known which contain both helium and lead. Strutt (later Lord Rayleigh) determined the ratio of helium to uranium in minerals from known geologic periods. Holmes and Lawson studied the ratio between lead and uranium content. From the figures thus obtained the age of the mineral concerned can be computed. It should be noted that the assumption is implied that in the long time since the formation of such a mineral no helium has been lost from it and that no lead was present in it along with the uranium at the beginning. If these postulates are not correct, of course no highly accurate figure for the age of the

mineral can be calculated. One would find too little helium and too much lead, the helium figure would give too low an age and the lead figure too high an age. And so we do find differences between the two values in the table given below, of the mean value for age found, in *millions of years*. Under He is the figure determined from the helium content, and under Pb is the figure from the lead content:

Geological period	He	Pb
Lower Precambrian	590	1500
Middle "	380	1300
Upper "	267	1200
Silurian	234	450
Devonian	120	300
Carboniferous	137	320
Permian	41	—
Old Eocene	26	—
Miocene	6	—
Pliocene	1.6	—
Pleistocene	1	—

The atomic weight of lead arising from uranium is 206 while that of ordinary lead is 207. By determination of the atomic weight of the lead to be found in a mineral, it can be calculated how much ordinary lead it already had, and how much new lead has formed, and thus the figures for the age can be corrected. In the table given above, the work of Lawson, the figures given are so corrected for this reason. Probably the figures given under the lead column are much nearer correct than those from the helium measurement.

In any case the geologists were correct in their surmise of the greater length of time necessary. In the Pre-Cambrian period no certain evidence of life on earth is to be found. But that a solid crust must have existed is certain because of the evidence furnished by shales from this period, which are to be found in Scandinavia and in North America. The Finnish geologist, Sederholm, considers it likely that a part at least of the graphite grains to be found in such deposits are of organic origin. In the Cambrian period, which is believed to have

lasted as long as have all the periods which have followed, taken together from the Silurian to the present time, definite organisms are found. They are even scatteringly found in the lower Cambrian. So organisms can be stated to have existed on earth for at least one thousand million years, and naturally it has been a yet longer time since the oldest portions of the earth's crust formed, and the first water gathered itself together in an ocean.

Chapter VII

ORES AND FOSSIL FUELS

In the previous chapter we considered the development of the solid layers of the earth in a general way, without a special study of their usefulness. Iron ores, because of their wide distribution deserve special mention. The definition of the word *ore* takes into account the value of the material. Only those metal compounds are called ores from which the metal can be won economically. Thus pyrite which is an iron mineral, is not called an ore, for the amount of iron got from this mineral under present day practice, has never reached a high value. The same ores may form in different ways and so may get several different names. Ore found in layers in sedimentary rock, called bedded ore, is widely distributed, but of comparatively little thickness. Thus there are layers of copper pyrite, or copper glance, of knife-blade thickness at Dyas near Mansfeld, Germany, in the Hartz mountains. To such ores belong the bog-ores and iron ochres which are to be found scattered in great layers in younger geological formations. Here too belong the great deposits of minette ores in Lothringen and Luxemburg, in one of the recently fought-over regions. Also to this group belong the important clay-iron deposits, iron-spar or siderite, found inlaid in clay-shales.

If ores are embedded in crystalline rock they often have a lens or gland shaped form. Such occurrences are then called ore deposits. Of this type are the great iron ore deposits of the United States, Sweden, Russia and Algeria, all of great importance to industry. A third widely distributed form in which ores may occur is in lodes, gangs or veins which pass through the surrounding rock, following its stratifications for short dis-

tances. This is the commonest mode of occurrence for ores of the rare metals.

In the last chapter we described how the metals may come to be dissolved in water, carried to oceans or lakes, and there precipitated, often by the action of organisms. In this way deposits of calcium carbonate are formed. This mineral is not called an ore, for it is not used in the preparation of metallic calcium. But when solutions of other metals such as iron and zinc come into contact with calcium carbonate, the calcium is partly replaced by these other metals and then ores of such metals are formed. Iron and manganese oxides are formed directly from solutions of the metals. Such deposits, originally sedimentary in nature, lose their water content when acted upon by heat or pressure.

In magmas all the different metals are present and so it is from these that all the metal compounds to be found in nature have originated. When a magma cools certain components generally separate out, which can pass off as volcanic gases if they come into contact with the air. If they do not have free egress they gather in fissures and blow-holes. Such spaces form in the neighborhood of intrusive magma masses partly as a result of the mechanical action of these masses in cracking the rock into which they come, and partly by the contraction of the magma in cooling. Other cavities, such as those in limestones may result from the solvent action of water. It was shown in the previous chapter that loose earth such as sand always has interstitial room into which solutions can seep. The main constituent of the volcanic gases is water vapor, and water is also contained in the masses solidifying from the magma. Such water is called "young." It carries in solution the gases and chemicals which are to be found in volcanic exhalations, such as sulfur dioxide, carbon dioxide, carbon monoxide, silica, chlorides and sulfides of both light and heavy metals. Doelter and other investigators have shown that sulfides are soluble in water, especially if alkali sulfides are present. The presence of carbon dioxide also probably contributes to such solubility, and

here too boric acid and fluorides help. Such water, possessing great solvent action because of the high temperature and pressure and the content of acid vapors, hydrogen sulfide, carbon dioxide and boric acid, seeps into the interstices, which may connect with the open air, and which generally contain dissolved or included gases other than those of the entering solution. Part of the gases are driven out, and the region is somewhat cooled. The water can no longer hold in solution many of the bodies, so these precipitate and are deposited on the walls of the holes and crevices. Some of the carbon dioxide may be precipitated by lime or baryta as calcite or heavy-spar. Fluorides, especially the difficultly soluble calcium salt, *fluorite*, or fluorspar, are precipitated; silicic acid separates as quartz crystal, iron may precipitate in part as pyrite. These minerals are not ores, they are known as gang minerals. The iron may also precipitate as oxide, and this is considered as an ore. Thus tin may precipitate as oxide, (the tin ore, *cassiterite*), and copper, zinc and lead commonly precipitate as sulfur compounds. Antimony, arsenic and bismuth form sulfur compounds. Sometimes pure free metal is to be found in these ore veins, especially the noble metals, gold, silver and platinum, but also mercury, tin, antimony and bismuth. These native metals result from the reducing properties of gases which separate from the magma; they might form in the presence of carbon monoxide.

It may also happen that these young or juvenile water solutions if they seep toward the surface of the earth may meet other water solutions coming from the surface and containing quite different salts from those of the juvenile solutions, and also containing oxygen gas held in solution. Various chemical changes then occur. Very commonly, after veins of minerals have formed, water from the surface seeps down into the vein and changes the sulfides to sulfates by oxidation. Then the metals may be precipitated as carbonates or changed to oxide (especially in the case of iron). Such formations of iron oxide and of its hydrate, occurring in the upper layers of ore veins are

called *iron-cap* and are considered by miners as good indications of rich ore beneath. Sulfuric acid freed in the oxide formation may seep down into the gang and may exert very great solvent action both on the gang-minerals and on the rock-walls of the vein, and thus a great number of chemical changes can occur. If gold or silver ores occur nearby these may be left in metal form, or may be changed to chloride, for alkali chlorides are commonly present. Such minerals are to be found in the upper layers, under the iron-cap. Other metal sulfates undergo changes further down. Of these zinc and copper sulfates are very soluble; lead sulfate is less so. If silicates dissolve from the surrounding rock walls, silicates of the metals may form anew. If carbonates have come into solution, copper, zinc or lead carbonate may be formed. From these latter in the case of lead or copper, oxides may form. Still deeper down the metal sulfates may encounter unchanged metal sulfides, most commonly, iron sulfide. A chemical change can occur in this case such that the iron is dissolved out and is replaced by more valuable metals. In this manner ores are enriched by the oxidation processes of the upper layers of the ore gangs and then by solution and seepage into lower layers. Below the enriched part there may be found the less rich, original gang-ore. In this way some of the richest of ore-deposits, the "bonanzas," have originated.

Of equal value with ore deposits are the occurrences of coal and of mineral oil. The mode of formation of fossil coal was easily determined. Between deposits of the dead remains of plants, and graphite, a pure crystalline form of carbon, there are to be found all gradations, such as peat, lignite or brown coal, soft coal and anthracite. Wood may be looked upon as a typical, dead, plant substance. It is made up of two chief constituents, cellulose and lignin, in about equal amount and also contains lesser amounts of resin-like constituents and inorganic matter which form the ash on burning. These inorganic salts and the water contained in the wood are not taken into consideration in the table of analyses given below, copied from

Clarke's great work "Data of Geochemistry." Otherwise the analyses which show the percentage of carbon, oxygen, hydrogen and nitrogen, would not be comparable on account of the great variability of the ash and water content. Figures for cellulose and for lignin themselves are given for comparison.

	C	O	H	N
Cellulose	44.4	49.4	6.2	—
Lignin	47.1	47.0	5.9	—
Wood — mean value	49.3	43.4	6.2	1.1
Sphagnum moss	49.9	42.4	6.5	1.2
Light peat	50.6	42.6	5.9	0.9
Peat — mean value	54.1	37.3	6.8	1.8
Heavy black peat	59.7	32.6	5.5	2.2
German lignite	57.0	35.7	5.9	1.4
American lignite	74.9	18.5	5.3	1.3
Sardinian lignite	82.3	10.0	6.5	1.2
German soft coal	83.8	29.7	5.0	7.5
American soft coal from Pa., Md. and Va.	87.5	5.9	5.2	7.6
American soft coal from Ohio, Ind., Ill., Iowa, Mo.	82.9	9.9	5.7	7.5
Scottish soft coal	83.6	9.0	5.5	1.9
English soft coal	84.2	8.8	5.6	1.4
Anthracite, Welsh	92.7	3.1	3.4	0.8
Anthracite, Ural Mts.	97.5	1.6	0.6	0.3

Depending on the degree of change which the organic plant residues have undergone, the carbon content increases. The nitrogen content stays nearly unchanged, the hydrogen decreases, but not to any great extent until the anthracite stage is reached. Oxygen decreases about as the carbon increases, so that their amount taken together makes up about 93%, except in the anthracite coal, where it sums over 96%. The carbonizing process has gone farther in the most coally peats than it has in the poorest lignites, while the best lignites are equal to, or surpass, the poorest soft coals. Otherwise the series is very regular. Dried wood and dried moss are higher in carbon than are cellulose or lignin. Sphagnum moss is chosen because it is one of the chief constituents of younger layers in peat swamps. Its composition is very like that of wood, but generally the ash is higher. The heavier or older peats are remarkably high in nitrogen content. The peat usually contains much lime and

iron, for in peat-swamps layers of bog-ore are to be found. Humic acid forms in these swamps and this with lime and iron gives insoluble precipitates. In the upper fresh peat the original plant-forms can be seen quite well preserved, but the more-aged, darker peat is a fairly uniform doughy mass.

Lignite or brown coal is not always brown in color, but may be black. It is a comparatively young coal, from the Mesozoic or Tertiary formations. Fossil charcoal is often found, just like coal of a charcoal oven. It has been claimed that this arose from ancient forest fires, lighted perhaps by lightning or by volcanic eruptions. Lignites are very like ordinary soft or bituminous coal. The lignites include the rather hard and shiny black coal called *jet*, sometimes used for decorative purposes, and not at all similar in appearance to an ordinary brown coal. Lignite has a higher water content, generally 15–20% although not as great as that of peat (20–30%). It may contain lime, commonly in the form of gypsum, and iron as iron sulfide. Like peat it may contain humus bodies which are soluble in alkalies, sometimes the lignite can even be completely dissolved in ammonia. Soft coal is not dissolved to any noticeable extent in alkalies. Dilute (10%) nitric acid at 70° actively attacks lignite, but is without action upon soft coal. Anthracite-like coals arise from lignite as a result of "contact metamorphoses" where lava masses have forced their way into lignite beds, yet they are markedly attacked by nitric acid. Thus there appears to exist a fundamental difference between lignite and true coal. Various English cannel-coals have high nitrogen content, over 2%, although the carbonized remains of the fossil calamite plants of which they are composed do not themselves contain more than about one-half of one percent of nitrogen. It is believed that the high content of nitrogen arises from animal remains which were embedded in mud or ooze at the same time as the fossil plants and so protected from complete oxidation by the oxygen of the air. Very likely micro-organisms exercised a great influence on the chemical processes which brought about the changes of the plant residues,

just as is now the case in peat-bogs. Iron sulfide is often present in disagreeable amount, causing the spontaneous combustion of coal and producing evil smelling sulfur gases in the distillation or burning of such coal.

In the oldest coals, called anthracites, the content of carbon is over 90%. Coals found in the older geological periods such as the Silurian and Cambrian and in the Pre-Cambrian are remarkable in their high content of carbon. Their amount and frequency of occurrence is small. A Pre-Cambrian coal, called Schungite, from Schunga near Lake Oneng in Russia, contains 99% of carbon and $\frac{1}{2}$% each of nitrogen and hydrogen. Yet this coal is not a graphite, for it does not form graphitic acid when treated with concentrated nitric acid, as is characteristic of true graphite.

It is well known that coal when heated gives off a volume of gas which is quite valuable. The older the coal the less is the amount of gas which it will give off and the greater is the residue of coke. The gases which pass off are of many sorts, hydrogen, methane, and other hydrocarbons, nitrogen, carbon monoxide, carbon dioxide and a little oxygen. The three first named of these are present in greatest amount, and make up between one-third and one-quarter of the total amount of gas; next comes the carbon monoxide, varying between 2.5 and 7.5%, then the carbon dioxide, between 0 and 2.7%, while the oxygen content is not over 1%. Water also passes out in the distillation of the coal, and this takes up ammonia and salts. Commonly the ammonia is recovered as ammonium sulfate, and is of considerable value. The same is true of coal-tar which similarly distills off. It contains higher and aromatic hydrocarbons and also oxidation products such as the phenols. Sulfur vapors are also formed and these are taken up in special purification plants and are later made use of. A comparison might be made between these distillation products from coal and those from wood, when the latter is charcoaled. The wood gives wood alcohol, acetic acid and acetone as the chief products.

Coal may also develop gases in nature. Often this is the result of the action of micro-organisms, the great multitude of which, existing in peat-marshes, form nitrogen, carbon dioxide, and methane (marsh gas). The gases which develop in coal mines are a source of great danger to the lives of the miners both because of their poisonous action and because of the danger of explosion of the so called "fire-damp." Lignite develops carbon dioxide up to 90% or more of the gas given off, so it is not dangerous in this latter particular. In the gases from soft and from anthracite coals there is less carbon dioxide, though occasionally it is quite important (over 50%), while in place of it, methane, or occasionally nitrogen is chief constituent. The methane causes explosions when mixed with air and ignited.

The carbonization of the original plant residues, as we have shown, takes place so that the oxygen is gradually removed and carbon dioxide formed. Various hydrocarbons of high carbon content result, in place of the original carbohydrates and lignites. By giving off hydrogen and methane gas the hydrogen content of the coal gradually decreases. A process similar to this takes place when hydrocarbons are heated. Volatile hydrocarbons and hydrogen gas pass off, and the remaining hydrocarbons become less and less volatile, as they acquire a higher and higher content of carbon. The purest carbon formed in this way must still be looked upon as a hydrocarbon with a particularly low hydrogen content. Actual chemically-pure carbon only occurs in crystalline form, as graphite or diamond.

The various sorts of coal are used mainly as fuel, and their price runs parallel to the heat per pound that they can give. The heat value of pure carbon is 8,080 kilogram calories. The heat value of hydrogen gas, if the water formed passes off as a vapor, is 28,800 kilogram calories. Thus the higher the content of hydrogen in a fuel, the higher should be the heat value. But of course one must take into account the ash, which does not give any heat, and also the fact that heat is used up in driving off any moisture present. Below are given the fuel values

in kilo-calories, and the moisture and ash content, of some common fuels (taken from K. Sonden's "Forbranningslara").

Material	*Moisture*	*Ash*	*Fuel Value*
Pine wood	20%	0.5%	3,460
Birch wood	25	0.5	2,970
Peat (Laxå, Sweden)	24	7.2	3,550
Peat (Ankarsrum, Sweden)	18	2.0	4,530
Lignite ("Marie" briquetts)	10	6.0	6,350
Swedish coal, Skromberga	11	19.6	4,950
Swedish coal, Höganäs	10.4	5.6	6,190
Scottish soft coal	2.2	3.1	7,480
Newcastle soft coal	1.4	2.9	7,670
Anthracite coal	0.7	4.6	8,660
Gas coke	5.0	8.0	7,000
American petroleum	—	—	10,300
Baku petroleum	—	—	10,000

The fuel value of the coal is higher the further the carbonization has gone, as is shown by the table.

The liquid fuels are given last in the table. These have a very high fuel value because of their high hydrogen content (around 14%) and because of the absence of moisture and ash. Such fuel consists chiefly of hydrocarbons and has found immensely widespread use. The common petroleum oil of America formerly was obtained from Pennsylvania. The hydrocarbons which this oil contained belong to a series of which the simplest representative is methane, CH_4. This series of hydrocarbons all have the chemical formula (C_nH_{2n+2}) where n is a whole number, and they are all called by the group-name of "paraffins." In mineral oils from Russia and in California oils the principal products are hydrocarbons of formula (C_nH_{2n}), from which it can be seen that these hold less hydrogen than the hydrocarbons of the eastern American petroleums. Besides these hydrocarbons there can be found in all petroleums small amounts of hydrocarbons belonging to the benzol series, (C_nH_{2n-6}), where n is 6 or more. Also naphthalene, ($C_{10}H_8$) is present in the mineral oils of Burma and of California.

Sulfur is found in most petroleums as sulfur compounds, but the amount is generally small. Texas petroleum contains a little dissolved, free sulfur. A little nitrogen is also present in most petroleums, particularly in those of California, where nitrogen compounds may exceed 10–20% of the raw oil. Oxygen compounds occasionally are present in the raw oils.

The simplest of the paraffins from methane, CH_4, up to butane, C_4H_{10}, are of low boiling point; in the cases given, −164° C. (−265° F.) and 1° C. respectively. They are therefore gases at ordinary temperatures. They stream out from bore-holes in the earth in areas where mineral oil exists, and they are often gathered and carried in pipes for long distances to serve as a cheap fuel for industries, and for street lighting, under the name of *natural gas*. They consist chiefly of methane. On the other hand the highest of the hydrocarbons from petroleums are of so high a melting point that they are solids at ordinary temperatures. These may be found in nature free from their more volatile relatives, and are used as sources of solid "paraffin." Often they go under the name of *bitumen*, *pitch* or *asphalt*. Sometimes they are mixed in with rock material from which they can be melted or distilled. Hard varieties of asphalt contain large amounts of sulfur, between 3 and 10%, while soft asphalts contain less sulfur. Asphalt is used for paving. For this purpose coal tar is sometimes also used, modernly after the extraction of all valuable byproducts.

With regard to the origin of the hydrocarbons which occur in the earth, many hypotheses have been promulgated. It is well known that when carbides come into contact with water they form hydrocarbons, mainly acetylene. This hydrocarbon does not occur in petroleum, but by various chemical processes acetylene can in part change into other hydrocarbons. For example acetylene and hydrogen gas in the presence of finely divided nickel form mixtures of the hydrocarbons of the paraffin group. Calcium carbide if it is heated with ammonium chloride gives off various hydrocarbons. The famous chemist, Mendelejeff, claimed in 1877 that petroleum

oils originated from carbides, and especially from iron carbide, in the interior of the earth, when carbides came into contact with water. This theory was taken up by Moissan in France, who claimed, however, that part of the petroleum is of organic origin. Walden has pointed out that this must be the case, for some petroleums exert a turning action on the plane of polarization of polarized light, a property which appears only to belong to substances arising from living things. For the view that bituminous bodies like pitch are of organic origin, there speaks also the fact that they are to be found only in fossil-bearing layers. They are quite wide-spread in the Silurian and younger formations. The work of Engler has contributed to belief in their animal origin. He distilled fish oil at a pressure of ten atmospheres and with temperatures between 320° (6080° F.) and 400° (752° F.). He found in the distillate a number of paraffins similar to those in petroleum. A similar experiment had been made in 1865 by Warren and Storer, who in this way made both paraffins and olefines (C_nH_{2n}), also benzol derivatives, all similar to the hydrocarbons occurring in mineral oils. Distillation of oils from the vegetable kingdom gives similar results. Without doubt the view that the origin of mineral oil is organic and principally from animal matter has today the most adherents.

"It can scarcely be doubted," said one of the members of the Fuel committee of the British Association in 1916, "that large amounts of easily obtainable coal have been the essential material basis of our great progress in business and industry during the past century and have insured us our favorable place with regard to other nations, but it is now equally certain that we can no longer call upon any such advantage over our nearest competitors."

An inventory of coal of all sorts available down to a depth of 1800 meters was prepared by the International Geological Congress held in Canada in 1913. This world coal supply amounted to not less than 7,307,553 million tons, and it was divided in the following percentages among the nations:

Europe	
Germany	5.7%
Great Britain	2.6
Russia	0.8
Austria	0.8
France	0.2
Belgium	0.2
Other Countries	0.3
	10.6
America	
The United States	51.8
Canada	16.4
Other Countries	0.7
	68.7
Asia	
China	13.5%
Siberia	2.3
India	1.2
Other Countries	0.3
	17.3
Australia	2.4
Africa	0.8
Total	100.%

The world's use of fossil coal has rapidly mounted from 800 million tons in 1903 to 1000 million tons in 1908, and to 1250 in 1913. In 1920 it was 1305 million tons. Should one take for the future yearly use an average figure of 1500 million tons, then the world supply cannot last more than 500 years.

If the use by the great industries is calculated, one obtains the following figures of average production in million of tons in the periods of years given:

Period	*United States*	*Great Britain*	*Germany*
1900–1904	288.1	226.8	112.5
1905–1909	400.5	256.0	139.8
1910–1914	519.2	269.9	168.3

In the German figures lignites and brown coals are not included. Actually, with them, production in Germany was a little greater than is shown. The production in the United States was increasing about 6% a year till 1918. It was calculated for 1918 at 600 million tons. In 1921 it was only 440 million tons, but since then has again increased. German production increases 4% per annum and English production 2%. If this development goes on, in 20 years the German production will be at the same rate as the English production, at 420 million tons per annum.

In England these figures have awakened considerable thought. This is not to be wondered at, especially when it is

realized that Germany, should it reach the same rate of production as England, could draw upon its remaining supply for twice as long as could the great island kingdom. With a yearly usage of 400 million tons the German supply would be used up in 1000 years, while that of Great Britain would come to an end in 450 years, an extremely short space of time measured in terms of history.

The United States even with a production two and one-half times greater than its present production, or a billion tons a year, can peacefully expect a 4000 year period of use, not allowing of course for greatly increased exportation such as might occur if American mines become the only readily available source of such fuel. There is not the least doubt that the United States will hold and further secure its position as industrial leader of the world and this is made even more certain by the fact that North America is very well placed as compared to Europe in the matter of supplies of iron. Ninety percent of the world's known coal reserve lies in the United States and in China, in the ratio of 4 to 3 respectively.

The war and its aftermath have produced great changes in the ownership of coal supplies as well as in the production of coal in the European States. Germany has lost much of its coal, in the Saar and in Silesia; Russia has lost its large Polish mines, while the Austrian fields are largely in the hands of Czechs and Poles. Impoverished German-Austria is almost portionless in this regard. Most of the great mines of Northern France and Belgium were left in ruins as a result of the German invasion. Furthermore a great many of the coal miners were torn from their work, or fell in battle, or were incapacitated, or became unwilling to continue in this work as a result of war-training in new occupations. They have been replaced by unskilled labor and this has led to mine accidents and to an abhorrence of mining work. It has resulted in great strikes. The world suffers from a great lack of coal, especially since strikes for economic reasons in America have also tied up and hindered production there. It is unfortu-

nately likely that many years will pass before conditions over the world are again normal.

A very great part of the coal mined in England is more and more being sent out of the country. In 1870 about one-eighth was exported, but in 1913 one-third of the English coal went to other countries, and the value of this export was one-tenth of the total exports. In 1870 it had been but one-fortieth of the total exports. Just before the war 70% of all the coal transported on the sea was from England and it was mainly used for the fuel supply of merchant vessels. Hence if coal exportation is to be lessened, merchant marines will be injured. In any case the English coal-supplies must needs be used economically, and the by-products, especially ammonium sulfate for agriculture and coal tar for the dye industry must be better cared for than formerly.

Liquid fuels do not play as important a role as the coal supply. In 1919 Europe produced about 4.1 million tons, of which 2.7 million tons came from Russia, 0.7 million from Roumania, and 0.7 million from Galicia. Formerly the United States led the field with 39.3 million tons, but at the end of the last century it was put in the second place by Russia. However, as a result of the Russian debacle that land retired to a position in oil production below that of Mexico, which produced 9.1 million tons in 1919. Mineral oil is being used up much faster than coal. In 1921 the United States produced about 70 million tons of crude petroleum and 5 billion gallons of gasoline (14 million tons). In the three years before 1919 production increased immensely, but this was only possible by the opening up of new discoveries, (in Mexico, Persia, Canada, California, South America, etc.), and by new borings in the old districts. The yields from the old oil fields of Pennsylvania and New York have much fallen off. In 1880 the oil production of Pennsylvania neared its maximum. Van Hise calculated that, with the same increase in the use of oil as that at present going on, the oil supply of the United States will be used up in 1935, and even should the use of oil not increase in the future it

would not last to the end of the century. Later data, in 1921, places the time of failure, even with no increase in use, at 1953.

At present the United States uses about 67% of the world production of oil and its imports now exceed its exports. Further oil discoveries, as yet little worked have been found in Java, China, Japan, Kurdistan, and near Rangoon in the ocean off the mouth of the Irrawaddy. But even with these supplies we can only look sorrowfully into a future without mineral oil. At present no good substitute has been found for use in automobile and airplane engines.

The coal laboratories of Germany have chiefly concerned themselves with the preparation of oil from coal, and this became exceedingly useful during the war. By extraction of the coal with liquid sulfur dioxide they succeeded in obtaining from soft coal about one-half percent of a thick golden yellow mineral oil. Also it is possible to prepare a petroleum-like oil by heating with aluminium chloride, naphthaline, a product obtained in the manufacture of gas from coal.

The history of the development of the Pennsylvania production of mineral oil is very interesting. The Indians knew of the existence of petroleum oils in various waters in western Pennsylvania and they used it as a medicine. The white settlers followed the example of the Indians and bottled the oil, selling it as a universal cure-all. The consumption of this medicine was soon so great that the demand could not be met. An official named Drake happened to think that since the oil came from the earth it might be better obtained by boring a shaft. The result in 1859 was over-production. At that time there was a great need of illuminating oil. The mineral oil was sent to the famous chemist, B. Silliman, at Yale College. It was distilled and found that the portion which passed over between 100° C. (212°F.) and 300° (572°F.) could be used as a good illuminating oil. Thus the refining of petroleum began. For a time the portions below 100° and above 300° comprising half the distillate were thrown away. Soon it was found that the portion boiling above 300° could be used for lubricating

oil, and also from about 1870 use began to be made of the lighter oil, called naphtha. These lighter hydrocarbons were used for fuel, but until about 1900 the supply exceeded the demand. At that time the automobile was introduced. The volatile oil was needed for the motor (the gas engine), and a great change occurred. The naphtha suited the purpose well. In 1910 the demand for these light oils, also called "benzine," "gasoline," or "petrol," became so great that a search was made for a new material for their preparation. It had already been found that the portion of the petroleum distilling above 300° decomposes on distillation under high pressure. Besides naphtha-like hydrocarbons there are also formed hydrocarbons of very high boiling point, and these by distillation and decomposition become very like the asphalt of Trinidad. Very likely the natural asphalt results from an evaporation of the volatile constituents of petroleum in the course of thousands of years. The "cracking" process, as the pressure distillation is called, came into immediate use. The distillation is usually carried on at 5 or 6 atmospheres pressure, and a raw material is used boiling from 200° to 350°, usually "cracked" at temperatures between 370–400° C. (700–750° F.). The preparation of petroleum-like oils out of naphthalene, mentioned above, may be looked upon as a special case of the formation of naphthas from high-boiling hydrocarbons.

The same sort of care as that about the future of mineral oil needs to be taken although less urgently about almost all raw materials. Each industry seeks to force its production as high as possible to obtain the greatest profits and takes no thought of the possible circumstance a half or a whole century in the future. Statesmen, however, must use another yardstick. Historic time covers about 5000 years. That is only one short episode in the existence of mankind. A statesman can plead no excuse for letting development go to a point where mankind will run the danger of an end of these things in the course of a few hundred years. Legislation must be enacted. Nations seek to escape the calamity, each for itself. It is under con-

sideration that, if not absolutely forbidden, the exportation of petroleum from the United States ought to be made very difficult. In England a similar endeavor to control the coal situation is evident. It will also be necessary, however, to decrease the use of coal. Van Hise advocated that petroleum should not be used for illumination, since electricity can replace it, nor should it be used for heating purposes, for coal and electricity can take its place, while he suggested that for small motors alcohol might now be prepared in quantity. Whether or not the latter statement is correct may be doubted.[1]

Concern about our raw materials casts its dark shadow over mankind. Those states which lack throw lustful glances at their neighbors, which happen to have more than they use. Still more tempting is the desire for gain from lands on the other side of the seas, inhabited by uncivilized natives, with interest unawakened to guardianship. Historical research of the future will demonstrate how much desire for raw materials was a cause of the recent great misfortune whose effects mankind, or better, the so-called civilized nations, are still undergoing. It is clear that some day we must come to forbid national egotism, equally with the profit-seeking of industries, from seeking a solution of the problem of the proper use of raw materials. Mankind must finally come to the viewpoint that in every possible way it will spare these raw materials for the future and that it will make use instead of the great power for work poured out by the sun above us in apparently undiminishing amount; or else will use the sun indirectly by employing the energy which is collected together in the form of water-flow, and in the green plants; for these are sources which can renew themselves.

[1] ". . . we can do so only at a tremendously increased cost. . . . One would have to grow corn on an acre of Oklahoma oil land for about three hundred years to obtain a volume of alcohol equal in fuel value to a supply of gasoline produced in from five to ten years." This is from the report of Lane and Bauer, petroleum chemists of the U. S. Bureau of Mines. It is possible that by use of waste molasses and waste wood we could gain alcohol equal to from 8 to 16% of our present motor-fuel needs. But whence the other 84 or 90%?

Chapter VIII

THE CHEMISTRY OF WATER AND AIR

From a chemical viewpoint the most important naturally occurring substance is water. It covers three-fifths of the surface of the earth and, in the form of vapor, it is an important constituent of the atmosphere. Gathered together in clouds and precipitated as rain it supports life and brings about slow transformations of the solid earth crust, by solution and by erosion. The rain removes from the air small amounts of gases, among which oxygen and carbon dioxide dissolve various constituents out of the rocks and carry them down to the sea. Wherever the water sinks below the earth's surface it brings about similar changes. With the aid of the carbonic acid it dissolves many salts, for example calcium salts, and carries these at last out into the great oceans or into the salt seas that have no outlet, such as the Caspian Sea, the Aral Sea, the Great Salt Lake, and the Dead Sea. At the same time it mechanically carries along gravel and silt, which are deposited off the mouths of the rivers thus building bars and deltas. During the voyage to the sea the character of the dissolved salts is gradually changed. In general the total salt content increases with the amount of irrigated earth surface passed over. From cultivated land the water removes sulfates; here the potassium sulfate is retained, but the sodium salt is dissolved out. This process is of great importance to the plant world, for the plants have need of potash, but, in general, have little use for soda. Potash and soda are to be found in nearly equal amount in spring-water; the relative amount of soda increases little by little as the water nears the ocean.

Sea water is a mobile substance, carried by powerful currents around all the great oceans of the world, so that mixing takes

place very completely and its salt content is very nearly the same everywhere. The concentration does change a little; it is less where many streams empty out and thus dilute the sea water, as for example in the Black Sea, where the salts make up only two percent; and it is greater where much evaporation occurs and there is little inflow, for example in the Mediterranean, where it is 3.9%, and yet more in the Red Sea (4%). The water of the Baltic Sea is of low salt content. The Baltic must be considered as an inland sea. The mean salt content of all the oceans can be taken as 3.5%, the principal salt being sodium chloride. The composition of the salt mixture in the Pacific Ocean is given in the following table; a mean of seventy-seven analyses made by the Challenger expedition. The figures for the Atlantic are a mean of twenty-two analyses of samples taken between the Cape of Good Hope and the English coast, while the figures for the Baltic are for samples taken between Gotland and Oland.

	Pacific	*Atlantic*	*Baltic*
Chlorine	55.29%	55.20%	55.01%
Sodium	30.59	30.26	30.47
Sulfate ion	7.69	7.91	8.00
Magnesium	3.73	3.90	3.53
Calcium	1.20	1.24	1.67
Potassium	1.11	1.11	1.00
Carbonate ion	0.21	0.21	0.14
Bromine	0.19	0.18	0.13
	100.01	100.01	99.95

Included with the potassium content of the Baltic water, there is 0.04% of rubidium. Also in this latter analysis there should be counted 0.15% of other substances, iron, silica and phosphoric acid, which would increase the total figure to 100%.

Calcium carbonate precipitates from sea water partly as crystalline limestone, as one can see at the mouth of the Rhone river, or along the Florida coast, but by far the greater part is removed by organisms — corals, mollusks and pteropods. Their limy-shells and skeletons contain crystalline calcium carbonate. It is calculated that yearly 2300 million tons of chemi-

cal substances are precipitated in the ocean, of which the largest portion, about 1300 million tons consists of calcium carbonate, while of the remaining 1000 million about one-third is silica, which is removed by organisms, and the rest consists of about 280 million tons of magnesium carbonate, 60 million tons of potash, 75 million tons of iron oxide and various other related oxides, and a residue of sulfate, which for the most part becomes reduced to metallic sulfides. The carbon dioxide content of sea water varies with the depth. At the surface it amounts to about 43 mg. per liter. Below the surface it decreases rapidly so that at 50 meters depth (150 ft.) only 34 mg. are present per liter. At the bottom of the great deeps of the sea it again has increased to nearly 47 mg. per liter. One result of this increase in carbon dioxide concentration with great depth is that the flakes and shells of lime which are continually being produced by the organic life in the upper layers are generally dissolved on sinking into the lower layers of high carbonate concentration. At a depth of over 3000 meters (9000 ft.) no pteropod shells are to be found, while the more strongly built shells of globigerina are still present 5000 meters below the surface. On the ocean bottom less and less lime is to be found the greater the depth. At 900 meters the calcium content of the bottom mud is not less than 86%, at 4000 meters it is only 47%, at 6000 meters it is scarcely one percent, and in yet deeper regions there lies a red mud, colored by iron oxide.

Besides the carbon dioxide, other atmospheric gases are to be found dissolved in sea water. Of these oxygen is, like the carbon dioxide, of the highest importance for the continuation of organic life in the ocean. The absorbed gas contained in the sea water is lower, as the temperature becomes higher. Thus 15.6 cc. of nitrogen may dissolve per liter at zero degrees C.; this amount, at 40 degrees is decreased to half. Of oxygen at zero degrees 8.18 cc. are absorbed, at 36 degrees only half this amount. In the air 21 parts by volume of oxygen are present for each 79 parts of nitrogen, while the nitrogen and oxygen dissolved

in water are present in the proportion of 34 parts of oxygen and 66 parts of nitrogen, as may be calculated from the above figures. The oxygen is not only necessary for the organic life of the sea but is also of importance for the decomposition of the living matter which dies — for it oxidizes this to carbon dioxide. From these facts, we may clear up the reason for the distribution of carbon dioxide at various depths, noted above. In the upper layers where there exists a rich plant life, the content of carbon dioxide decreases rapidly with depth, from 43 at the surface to 34 at 50 meters. Below this, as plant life becomes less, it mounts again to 49 mg. at 90 meters; this increase results mainly, however, from the "burning" or oxidation of the dead organisms. The carbon dioxide content below this point decreases again, and at 200 meters depth is again about equal to that at the surface of the sea, so remaining until the bottom is approached, where it again increases, due to the influx of cold currents of water with a high carbon-dioxide content.

As a result of the oxidation process above mentioned, the oxygen is removed from the water, so that the content of this gas decreases rapidly with depth. Thus Buchanan found the following figures for the oxygen content of the gases dissolved in sea water at different depths of the Atlantic Ocean in the equatorial regions.

Surface	33.7%
at 370 meters	23.4
at 550 meters	11.4
at 800 meters	15.5
at 1600 meters	22.6
below 2000 meters	23.4

The increase at great depths is here again due to the influx of streams of cold water. In the Black Sea, where the salt-content increases greatly with depth, the cooling of the upper layer in winter cannot bring about any circulation of water below a depth of 50 meters. As a result no oxygen reaches the lower layers. The sinking decaying organisms in this sea must

oxidize at the cost of the sulfates, from the sulfur of which hydrogen sulfide is formed. Down to 90 meters the content of this impurity is not noticeable, but it increases below that depth rapidly, so that at 125 meters there are 71 cc., at 200 meters 215 cc., and at 500 meters 570 cc. of hydrogen sulfide (measured at zero degree and atmospheric pressure) in each liter of water. As a result of this fact, all life in this sea ceases below 90 meters. The case of the Baltic Sea is similar, though to a less degree; in many places such, for example, as in the deep which lies off Landsort, Sweden, formation of hydrogen sulfide occurs. Here however it does not go to such an extent that all life on the sea-bottom is killed. The hydrogen sulfide reacts with metal salts to form metal sulfides both in the water and on the bottom of the sea.

So we see that the salts passed by the rivers into the sea, become changed, generally leaving the final composition of sea water set forth above. The salts are given in the table as ions, which can combine to salts, this being the most useful way of setting them forth. It is possible to mix certain salts and so obtain artificially a similar solution to that which makes up sea water. Such a formula will be given here (after Dittmar):

Sodium chloride	77.76%
Magnesium chloride	10.88
Magnesium sulfate	4.74
Calcium sulfate	3.60
Potassium sulfate	2.47
Calcium carbonate	0.34
Magnesium bromide	0.22
	100.01

Naturally the sodium in sea water is present not only as sodium chloride but also as sulfate, and the sodium sulfate makes a greater amount than the potassium and calcium sulfate taken together. So also the sodium carbonate and sodium bromide are present in greater amount than are calcium carbonate and magnesium bromide. The composition of sea

water expressed in the manner which Dittmar and others have employed is quite incorrect for the actual salts present, and it has therefore been found better to give the salt content of a water in terms of the ions present. If one wishes to make up an artificial water, for an aquarium for example, it can be done by following Dittmar's table, so sometimes the old way of expressing the matter is the more useful. But one would expect from Dittmar's table that $\frac{7}{8}$ of the salt content of sea water should be obtainable in the form of sodium chloride. As sodium chloride is, to man, the most important of the salts — an adult uses yearly 5 or 6 kilos — mankind has from a very early time made use of sea water, because of its high content of common salt (2.7 percent) for the preparation of that salt. In former times, when it was not necessary to count the cost of heat, they boiled away the sea water until the common salt, which is but little more soluble at a boiling temperature, precipitated out. Since the other salts remained in solution, a product was thus obtained which was but slightly contaminated with these substances. If the evaporation was carried further the other salts finally began to come out, namely the salts of magnesium, and contaminated the common salt. It was then said that the "salt had lost its savor."

But today no salt is prepared by boiling. In southern lands, with their strong solar radiation, the sea water is run into shallow basins and is evaporated. Great plants of this type are to be found at Cadiz and Figuerras in Spain, at Setubal in Portugal and at Cagliari in Sardinia. The water is first let stand in clearing basins, then it is run into a row of evaporation basins in which gypsum and potassium and magnesium sulfate crystallize out. Next it is led into other basins, where the major part of the common salt is obtained. The remaining mother liquor, which contains principally magnesium chloride, is flowed or pumped back into the ocean. The impure salt obtained in this way is piled up in heaps. The content of magnesium chloride causes it to take up moisture from the air, and little by little this impurity goes into solution and flows

away, so that the salt is partly purified. Salt thus obtained is marketed, though it still contains from 3 to 7% of impurities, including its moisture. If one wishes to have highly purified sodium chloride this product must receive further treatment. Common salt is one of the most important of chemical raw materials.

A similar evaporation of sea water has taken place in nature over great areas and in this way the great salt deposits have been formed. Of these the greatest is at Stassfurt in Prussia. In the southwestern states of the United States in recent years other great salt deposits have been found. In 1849 Usiglio studied the order of deposition of the salts from Mediterranean water taken at Cette. He found that the salt could be made use of only when evaporation was not carried beyond one-fortieth part of the original volume. The salt content of Usiglio's original material was 3.77 percent.

Some remarkable researches were made by van't Hoff and his pupils to gain knowledge about the salt-layers which were coming to have great value in industry and agriculture. Thirty different salt-minerals are to be found in these salt layers. They consist mainly of chlorides. Second in importance are sulfates. Present in smaller amount are borates and carbonates (limestone) and still less bromine and iodine-containing minerals, ammonia compounds and nitrates. Copper and helium are also present. Van't Hoff studied the manner in which these minerals of the Stassfurt deposits might have come to exist. The determining factors for the precipitation of a salt from a solution are the chemical composition of the solution, its temperature and to a less degree the prevailing pressure. The actual influence of changes in this latter factor has never been studied. The researches of van't Hoff and his co-workers were carried out at ordinary atmospheric pressure. Van't Hoff found that the effect of temperature gave interesting results. Salt-minerals could not precipitate from a salt solution if the temperature was lower than those here given:

Glauberite, $CaSO_4$, Na_2SO_4	10°C.	50°F.
Langbeinite, K_2SO_3, $MgSO_4$	37°C.	98.6°E.
Loewite, Na_2SO_4, $MgSO_4$, $2\frac{1}{2}H_2O$	44°C.	111°F.
Vanthoffite, $3Na_2SO_4$, $MgSO_4$	46°C.	115°F.
Loewite with Vanthoffite	60°C.	140°F.
Keiserite with Sylvite	85°C.	185°F.
Langbeinite with Keiserite and Sylvite	72°C.	161.6°F.

Van't Hoff called these salt combinations a "geologic thermometer" and set it down as a rule that if the last of the above named combinations occurred in a salt deposit, then the temperature of formation of the layer in question must have been 72–85°C. But this is very unlikely. For various geological reasons we must conclude that at the time of formation of the deposits the temperature of the earth's surface in such areas was not very much greater than it is now. An alternate possibility to van't Hoff's theory is that the salts in question were thrown out of sea water at a temperature below 20°C. (68F.). Then they were covered by sediments and as a result the temperature rose. It increases about 30°C. for each kilometer of depth. A covering of about $2\frac{1}{2}$ kilometers would thus bring about a temperature of over 85°C. (185°F.) so that the above mentioned changes could occur and langbeinite, keiserite and sylvite could make their appearance. Water would be freed, and some of the salts would dissolve in this and then it might pass out to the surface. When later the temperature again became lowered to its present value, the old mineral salts could not again form, for the necessary salt-solution had been carried away, or had diffused away into other layers. There are various good indications that the calcium sulfate found in these salt layers originally was precipitated out with water of crystallization, i.e. as gypsum, and this would indicate that the temperature of the great salt sea from which the deposits originated was not over 25°C. (77° F.). It may even have been as low as 10–20° C. (50–68° F.).

Borings to 1460 meters depth in the deposits of immense area around Sperenberg near Berlin have never succeeded in passing

out of the salt-layer. Such deposits stretch over a surface from Alsace to northern Hanover and to the borders of Silesia and Poland. The salt sea from which they originate must have covered an area of about 100,000 sq. miles. The great quantities of salt and gypsum indicate a depth of sea water over this area of about 100 kilometers. Actually however this sea could

FIG. 17. KARABOGHAS OR KARABUGAZ BAY.
A PRESENT-DAY LABORATORY OF NATURE.

not have been over one kilometer (five-eighths of a mile) deep on the average, so the evaporation must have taken place over a very long period of time and the water must finally have collected into lakes where the crystallization finally took place. An example from our present day which throws light on this problem is furnished by the Bay of Karaboghas on the

eastern shore of the Caspian Sea. Because of the rapid evaporation and because there is no inflow of fresh water from the lands around this bay, a current is continually flowing from the main body of the Caspian into the bay, and a salt mass of not less than 350,000 tons per day is added to the deposits on the floor and margins of the bay. Its water is so salty that no life exists and masses of salts actually form and precipitate in the water. On the shore, crystals of gypsum form, and in the winter time also sodium sulfate — this latter partly re-dissolves in summer when the water is warmer and can hold it in solution. Sodium chloride, which of course makes up the main bulk of the mineral matter present in the water, is still held completely in solution. See map, Fig. 17.

The salt layers of Germany have been used since the thirteenth century and were probably worked for common salt at a still earlier date. Many springs in this region were very high in salt content, and their salt was crystallized out in so-called grade-works. At a later time borings were driven to the salt layers and salt water was pumped out. Finally in 1843 near Stassfurt a shaft was sunk to the solid deposits. The upper layers contained so much magnesium that the salt could not be made use of. This was called "abraum-salz" (German for "trash"), and was thrown away. Later it was found that these were the most valuable layers, because of their high potash content. Today they form the chief raw material for potassium salts, of the highest importance both in agriculture and industry.

Search for potash deposits outside of Germany have been rather unsuccessful. In the old salt works, dating from Roman times, at Cardona in Spain, potash salts have recently been found. They have been purchased by the French. Of their value one can as yet say little. In the Argentine at Leoncito there occurs a rock salt containing 17.5% KCl. Also various algae have the ability to remove potassium salts from sea water. In the United States attempts have been made to get potash from the ash of these sea-plants, but the results do not

appear to be of any great economic success. The process which appears to be most desirable at the present time for potash manufacture, next of course to the actual mining of potassium salts, is the recovery of dust from cement factories.

The same relation as that of the world ocean and the rivers which flow into it, holds for the salt-seas and their tributary streams. Of course the special nature of these streams determines the composition of salts to be found in such seas.

The well known Great Salt Lake in Utah has a water very like that of the world ocean. The salts contained therein are of a little greater sodium and potassium content, but have a little less magnesium, sulfate, bromide and carbonate, than the ocean. The salt content is increasing rapidly; in 1913 it was 20.3 percent. In the western states of America, Nevada and California especially, various strongly alkaline lakes may be found, such as the Great Soda Lake in Nevada, and the Borax Lake in California. These contain mainly common salt, but also large amounts of soda, and in the latter case, considerable borax. Many of these lakes are worked for soda and borax. Similar lakes occur in South America, Asia and Africa.

The greatest isolated sea is the Caspian. At the mouths of the great rivers, the Volga and the Ural, which empty into it, the water is only slightly brackish and the average salt content is only 1.3 percent if one omits the bay of Karaboghas, mentioned above, where it may reach a figure of over 29 percent. The Aral Sea has water very like that of the Caspian but with more sulfate and less chloride. Both these seas have more sulfate, magnesium and calcium than the ocean, but have less sodium and less chlorine.

The Dead Sea is of quite a different nature. There the salt content increases from 19 percent on the surface water of the northern end, up to 26 percent at 300 meters depth at the southern end, at Ras Feschkah. For comparison we will give here analyses from the main body of the Caspian, from Karaboghas Bay and from the two places mentioned in the Dead Sea:

	Caspian	*Karaboghas*	*North end Dead Sea*	*South end at 300 m. Dead Sea*
Chlorine	42.04%	53.32%	65.81%	67.30%
Bromine	0.05	0.06	2.37	2.72
Sulfate ion	23.99	17.39	0.31	0.24
Carbonate ion	0.37	—	—	—
Sodium	24.70	11.51	11.65	5.50
Potassium	0.56	1.89	1.85	1.68
Calcium	2.29	—	4.73	6.64
Magnesium	5.97	15.83	13.28	15.92
	99.97	100.00	100.00	100.00
Total salts in percent	1.294	28.50	19.22	26.00

The principal difference between the salts of Karaboghas Bay and those of the Dead Sea is the nearly complete absence of sulfate from the latter — made up for by chloride. Calcium salts are lacking from the former while they are abundant in the Dead Sea. In both places carbonates are lacking. The high bromide content of the Dead Sea might also be noted.

The salts which deposit out from such seas naturally have a composition which depends on the composition of the salt water. Some of these seas dry up completely in the summer, — thus it is with many that are to be found in Nevada and California. From the Soda Lake at Ragtown, Nevada, neutral and acid sodium carbonate crystallize out, with an impurity of 2 to 3% of sodium chloride and sodium sulfate. It consists mainly of a salt called trona, Na_2CO_3, $NaHCO_3$, $2H_2O$. This salt is harvested on a large scale from such lakes as Owens Lake in California. So also certain lakes in California are used for the harvesting of borax, which crystallizes from them. According to Becker the material probably originates from nearby springs of volcanic origin. These contain not only boron salts but also ammonium salts as characteristic constituents. The same is true of the volcanic vapors from various fumaroles in Tuscany the products of which are used for industry. The steam from such Italian fumaroles is also used to drive steam engines. Recently a similar installation has been made in California. In various other places such as Yellowstone Park and in Venezuela hot springs have been found which

contain boron salts and ammonium salts. Also in the borax deposits of Thibet, which originated from hot springs, and have been worked for ages, there are to be found ammonium salts and sulfur, which often accompany such deposits. In the California deserts, however, nitrates take the place of ammonium salts in the boric acid deposits. Of course this is also the case in the great deposits of soda saltpeter (sodium nitrate) in the Tarapaca and Atacama deserts of Chile, and in the borax deposits of the Argentine, and the potash saltpeter deposits of Cockabamba in Bolivia.

Nitrate is extremely valuable. It originates in nature as a result of the action of micro-organisms on organic substances containing nitrogen. In damp regions the nitrate is dissolved as formed and used by plants. Therefore large deposits of nitrate occur only in dry or desert regions. The greatest deposits of nitrates are those of the Atacama and Tarapaca deserts, above mentioned. Other nitrate deposits occur in Bolivia, Columbia, and the Argentine. Of the origin of these extremely important deposits many views have been hazarded. Very likely they are of volcanic origin but organic products which have been decomposed by micro-organisms have played an important role in their formation.

Above the ocean and the solid earth-crust lies the atmosphere. This is composed of a few gases of which nitrogen and oxygen make up the main mass, namely 78.1% and 21% by volume. The residue is made up of the so-called noble gases, — chemically inert, among which the chief is argon. The others occur in still smaller amount: krypton, xenon, neon and helium. These rare gases have no part to play in nature's house-keeping. They are occasionally made use of to fill electric lamps, and helium is coming into use in the United States as a non-explosive filling material for balloons and dirigibles. Besides the above-named gases there are to be found in the air small amounts of water vapor and carbon dioxide.

In recent times the nitrogen of the air has been of considerable use in industry, for means have been found to "fix"

it in the form of nitric acid or ammonia or calcium nitride, and these latter substances are of great value in agriculture and industry. Nitrogen gas itself is not a particularly valuable chemical for it occurs everywhere in the air, and can be used in as large amounts as is desired, since fresh gas will always stream in as fast as it is used up. But to get pure nitrogen gas from the air the oxygen must be removed by combining it with reducing substances such as phosphorus — or else the air must be liquified as described below.

Oxygen is a very important chemical because of its activity. It is used in many industries. Since it makes up 21% of the air, and because it is often desirable to have it in a more concentrated form, it is extracted from the air nowadays by cooling the latter and compressing it. Oxygen then separates out as a liquid at a higher temperature than does nitrogen. In this way the two gases can be separated from one another and concentrated. The water vapor present in the air, and the carbon dioxide are very important for plant life, and therefore for all life on earth. The same is true of the oxygen.

Tiny amounts of still other gases such as hydrogen have been found in the air. In the uppermost air layers hydrogen must play an important role. Methane, carbon monoxide and sulfur dioxide are also sometimes present in the air. The last named gas arises from the burning of coal containing sulfur or pyrite (iron sulfide).

Electric charges in the air cause the formation of ozone, nitrous acid, nitric acid and ammonia. These gases, though they only occur in very small amount, are quite important, especially the nitrogen compounds, because they are carried down to the earth by the rain water and are taken up by the plants.

Very likely the atmosphere formerly had a very different composition from that which it has at present. Doubtless when the earth had a temperature above 1200° C. (2200° F.) so that a solid crust had not formed, the gases of the outer layers were of the same type as those at present to be found in the outer layers of the sun. These include metal vapors, carbon and

carbon monoxide, hydrogen in great quantities and oxygen, nitrogen and the rare gases, especially helium. On cooling, the oxygen began to be taken up by the metal vapors and, if any oxygen was left over after this, by the hydrogen. One can get some idea of the former, primal atmosphere by considering the vapors emitted by volcanic craters. With the common gases occur also various acid vapors, such as CO_2 and SO_2 and a little HCl. These vapors combine with the newly formed metal oxides, forming carbonates, sulfites and chlorides, and the sulfurous acid salts become reduced to sulfides. The chlorides are now to be found in sea-water. The metal sulfides and carbonates are precipitated as minerals. Part of the carbonic acid has passed into the atmosphere, of which at one time it made an important constituent. Later, when a solid crust had formed, nitrogen and the rare gases, hydrogen and carbon dioxide were present in the air, but there was probably little oxygen. By the life processes of plants, some of the carbon dioxide gradually was changed to the carbon compounds which make up plant materials, and finally came to form the beds of peat, coal and other fossil carbon. It has been reckoned that the coal laid down in the earth is about chemically equivalent to the oxygen nowadays to be found in the air. The carbon dioxide consumed from the air has of course been replaced in part by volcanic exhalations. The used-up carbonic acid has mainly gone into the formation of limestone and other mineral carbonates — not even one full percent of it has been converted by the action of plants into the useful fossil fuel. The metabolism of plants is so intensive that it has been calculated that in thirty-seven years' time, the plants could use up the entire carbon dioxide content of the air. But actually in the burning and decay of plant material the same amount of carbon dioxide is returned to the air as was used in the formation of this material, if one excepts the very small portion which goes into the formation of beds of peat or fossil coal. Oxygen, carbon dioxide and water vapor are the lifegiving and active constituents of the air. The bulk

of the air — the nitrogen — is much more stable, but it too takes part to some extent in Nature's cycle. Electric charges in the air form small amounts of nitrogen compounds and these are carried down to the earth's surface and used as very necessary foods by the plants. Certain plants, and especially certain bacteria can use directly the nitrogen of the air, and so can bring this element into the general circulation or cycle upon which life depends.

Chapter IX

SOURCES OF ENERGY

It has been shown that when a chemical reaction takes place between two or more substances, new substances result which often show properties very different from the parent chemicals. Thus by the combination of the greenish-yellow gas, chlorine, with the light and soft metal, sodium, there is formed the very well known substance, common salt, which in nowise displays any similarity to either parent substance.

It is this fact which is the basis for the unending richness of varied materials with sharply differentiated properties which chemistry can provide us. Not only does matter change in chemical processes, but also the energy content changes. This commonly displays itself as a development of heat, and often such heating is of the greatest importance, for example in the process mentioned above, when 35.5 gms. of chlorine combine with 23 gms. of sodium to form 58.5 grams of sodium chloride, no less than 97,690 gram calories of heat are set free. A gram calory is one one-hundredth of the amount of heat which is needed to warm a gram of water from zero to 100° C.—i.e. from the freezing to the boiling point. So this amount of heat which is freed in the formation of salt would serve to warm 977 gms. of water, that is about two quarts, from zero to 100° C. Sometimes it happens that during a chemical combination the heat development may be negative. Thus for example 5,520 gm. calories disappear when 197 gms. of gold combine with 127 gms. of iodine to form gold iodide. Such a process will not take place at ordinary temperatures by itself, but only in a roundabout way, through a series of other chemical processes and not by direct combination of gold and iodine. This rule holds so generally that the thermochemists, men who sought to study

the amounts of heat energy developed in chemical processes, at one period claimed that no chemical reaction could take place if heat was not set free in the process. Among such chemists were the Frenchman, Berthelot and the Dane, Julius Thomsen, who both tried to establish the truth of such a theory. That it is not true can be readily demonstrated from the fact that the heat of solution of most salts in water is negative; that is to say when a salt dissolves in water a cooling effect is generally noticeable. Thus for example when 58.5 grms. of sodium chloride are dissolved in water there is taken up from the surroundings 1,180 gm. cal. This corresponds somewhat to the heat disappearance which takes place when ice melts, for one must add 80 gm. cal. of heat to one gram of ice to change it, at zero degrees, to one gram of water. Use is made of this fact to obtain very low temperatures by means of the so called freezing-mixtures. A mixture of ice and salt is often used in the household, for example in making ice-cream. In such a mixture heat is taken up both for the melting of the ice and for the solution of the salt in the ice-water. With this mixture the temperature can be lowered to about 20 degrees below zero C. Still more effect can be obtained from a mixture of snow and calcium chloride, going to as low as $-50°$. Such facts made it seem unlikely that the old thermochemists were right in stating that all chemical processes developed heat. They replied that dissolving a salt in water was not a chemical process. However the debate has long since been decided against these claimants. They were right to this extent, that most chemical processes which will take place at low temperatures, such as ordinary room temperature, are accompanied by development of heat. But, as a consequence of one of the laws of thermochemistry set forth by Le Chatelier and van't Hoff, the circumstance is different with higher temperatures, so that the higher the temperature, the better can occur those processes in which a disappearance of heat is concerned. Therefore we use high temperatures to prepare bodies with a high energy-content, as for example

in the preparation of ozone from oxygen, of calcium carbide from lime and charcoal, of oxidation products of nitrogen from the nitrogen and oxygen of the air, etc.

It is just as important for the continuation of civilization and culture that heat should develop from certain chemical processes as it is that the properties of matter should change in a chemical process. We need only remember that fire really only serves man by supplying him with heat and light, and, here also the development of light may be looked upon as a special case of energy-development. Think, too, of our factories and our modes of transportation, for the most part driven by energy developed by the burning of coal in fire-boxes under steam-boilers.

A long time ago men came to the conclusion that all energy must ultimately come to us from the sun, and therefore this body was worshipped as the All-father, the Giver of all Good. Science also teaches that practically all the energy to be found upon earth originates from the sun, with the possible exception of the energy developed by the tidal phenomena, which arises from the rotation of the earth upon its axis. But even this exception need not be made, for doubtless the rotation of the earth results from the motion of the spiral nebula out of which the earth gradually became separate from the principal mass, which latter became the body of the sun. The heat which we obtain by burning wood, peat or coal all originated from solar heat, so these fuels can be looked upon as storehouses of the solar energy, and so too we may consider the food materials with which we maintain our lives.

The amount of heat yearly radiated out into space from the sun is enormously great. It is not less than 1.55 gram calories per gram of the immense solar mass of 19×10^{32} grams, i.e., 19 with thirty-two naughts after it or 1,900,000,000,000,000,000,000,000,000,000,000. The yearly loss of heat from the sun is thus more than 3×10^{33} gram cal. Onto the earth only 1/2260th millionth part of this comes, or in other words 133×10^{22} gram cal. Of this amount of heat which the

earth does receive, the plant-world takes up but a little. According to the calculations of H. Schroeder, the plants yearly change 60 billion kilograms of carbon dioxide to organic substances. For each gram of carbon dioxide there can be taken a heat figure of 2,200 gram cal. So on the whole earth surface, there come to be used in this way 132×10^{18} gm. cal. or 1/10,000th part of the solar heat received on the earth. From this figure may be subtracted the amount of heat yearly developed by the burning of fossil fuel which, taking the annual coal output at 1500 million tons, would be about 12×10^{18} gram calories or only 1/11th of the solar heat used by the plant world. Schroeder reckons that of this solar heat 67 percent falls on the forests, 24% on cultivated vegetation, 7% on the grassy-steppes and prairies, and 2% on wastelands such as deserts, polar regions, etc. This unthinkable quantity of heat lost yearly by the sun, 3×10^{33} gram cal., appears to have been radiated year after year in nearly unchanging amount over the whole period of time that life has been in existence on earth, as can be concluded from the remains of organisms which are to be found in the geological strata. This period of time may be roughly estimated at a billion years. So the sun must have a source of energy of dimensions unthinkable for us. Doubtless this energy arises for the most part from chemical processes taking place in the sun, and rather similar to the radioactive changes which we know on earth — for these latter develop far greater amounts of heat than do any other processes of chemistry known to us.

In any case as huge as they seem to us, the amounts of energy which are used to the benefit of the life of the earth, are only very tiny portions of the total heat which comes to us from the mighty sun. The great deposits of fossil coal which lie in the earth are estimated to correspond to 8,000 billion kilograms of carbon dioxide or 133 times the yearly consumption of carbon dioxide by the plants, and so about 1500 times the annual consumption of coal by man. Since we have every reason to hope that mankind will continue in existence for a

far longer period than another 1500 years, we must prophesy that our descendants, even should they succeed in making use of every gram of fossil fuel, will have to get along without this source of energy after another fifteen centuries, (and this is without figuring on any increase in consumption of coal). But by far the greater part of the fossil fuel lies so placed in the interior of the earth that we cannot count upon it's ever being brought to the surface. The actual coal supply will thus come to be used up in a much shorter space of time. It has been reckoned that English coal will be used up in 400 years and the coal supply of the United States, which is the best provided of all the civilized lands in this respect, has been figured will fill the needs of that land for about 4000 years, even with some slight increase in the use of coal. But if this increase is to continue in the rapid way which it has done in the recent past, the coal will be used in only 150 years, and in England in perhaps only fifty years. It is evident that very shortly mankind must modify housekeeping methods, and discontinue his present prodigal use of coal.

Another source of energy, which, for countries like Sweden and Canada, is of greater importance than coal, is that of water power, i.e., of hydroelectric power. To compare the usefulness of a steam power unit with an electric unit, we can show that the development of one horse-power-hour corresponds to the use of 2/3rds of a kilo of coal. We must also assume that the work done is continuous, i.e. continues for a whole year or 8,796 hours. A horse power year then corresponds to a coal consumption of 5,840 kilos, in round numbers to 5.8 tons of anthracite. In reckoning water power one can consider that if a water-mass of a cubic meter per second falls from a height of a meter it can furnish a horse power of work. One million horse power of energy can take the place of 5,800,000 tons of coal, used in the best steam engines known to us today. But how much water power is available? This question can be answered in many different ways, depending on whether or not the source of water is very variable at different times in the

year. Thus for example the total fall of water over Sweden can furnish about 10 million horse power over six months of the year, but if the period of use is nine months of the year, only six and three-quarters million horse power can be obtained, and still less if the power is spread over the whole year. Nine months use is commonly counted as the practical value as a basis for calculation, and the corresponding power is called "the water supply of industrial mean-water." The water which could be obtained by wise conservation might be slightly greater than this figure. Below is given a table of the available waterpowers of industrial mean-water of the more important industrial lands in Europe and America, from the calculations of Koehn and Kaplan:

	Horse power	*h.p. per inhabitant*
Canada	26,000,000	4.
United States	100,000,000	1.
Norway	7,500,000	3.
Sweden	6,750,000	1.17
Finland	2,600,000	0.8
Iceland	2,000,000	22.
Switzerland	1,500,000	0.4
Italy	5,500,000	0.15
Spain	5,200,000	0.26
France	5,860,000	0.15
Austria-Hungary	6,130,000	0.12
Russia	3,000,000	0.02
Germany	1,426,060	0.02
Balkans	10,000,000	0.6
Great Britain	960,000	0.02

The distribution by continents is as follows:

	Millions of h.p.
Europe	59
Asia	236
Africa	160
North America	160
South America	94
Australia	30
World Total	739

From these tables it may be seen that North America is extremely well situated, especially if we also take into account

its other forms of natural wealth. In Europe, the Scandinavian countries with the exception of Denmark, are best situated and Norway is particularly well off. Then come the Alpine regions and Italy, while the Balkans are also very well provided. Far down the list stand the low-lands, Germany and Britain, which have been forced to develop their industries with the use of fossil fuel. In sum the whole of Europe can only furnish about 60 million h.p. or about 60% of the supply of the U. S.

If one reckons a supply of about 300 million h.p. over the civilized portion of the globe, this corresponds to a yearly use of 1740 million tons of coal or a figure slightly greater than the present rate of consumption of that fossil fuel.

Of course the other parts of the world possess water powers of great importance. For example the Victoria falls of the Zambezi River (119 meters high) could furnish 35 million h.p. or five times as much as does Niagara. Likewise there are great water-falls in South America which are not taken into consideration as yet. The smaller table gives a calculation of the available power in all parts of the world, and these approximate figures total a world-summary of 739 million horse power.

Thus it would appear as if water power ought to replace steam engines fired by coal. This is not possible, however, because, in Sweden for example, as early as 1897 the industrially used water powers had exceeded the corresponding heat-powers by 69 percent, and in 1916 by 91 %. Water power in use increased from 207,000 to 925,000 h.p. but heat powers also mounted from 123,000 to 481,000 h.p. So it may be seen that water power has increased in somewhat greater degree than had steam-power, but this development came largely in two war-years of 1915-16, when there was a crisis of high fuel prices, while during the years from 1897 to 1914 the industrially used steam powers had grown in greater proportion than the water powers.

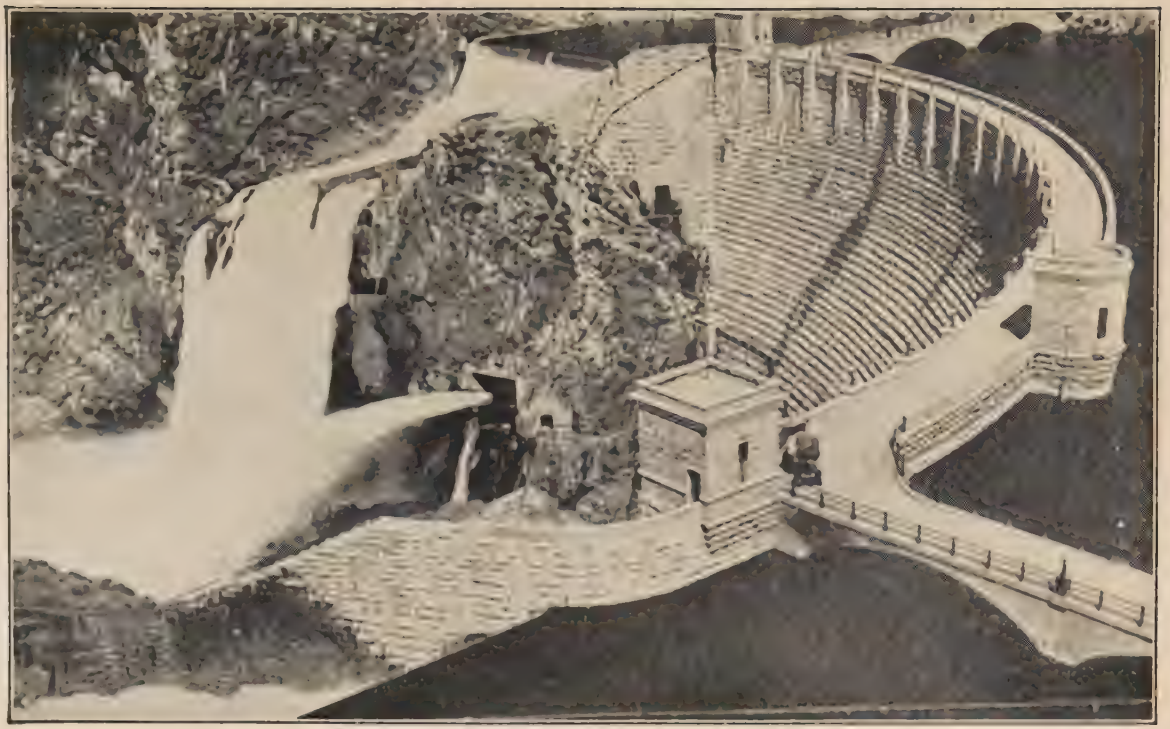
One of the great difficulties in connection with the practical use of water powers is that the water-falls lie in districts often

far from lines of communications, and in places where the erection of factories is impossible. However there still exist many falls of serviceable heights and power, which can be developed. According to the calculations of M. Serrander, for example, in Sweden such developable powers could furnish more than 3.5 million horse power, and of these more than two thirds, or 2.44 million, lie in Norrland and Dalecarlia. The portions of Sweden which are most important industrially, middle Sweden and Skåne (in the south) are very poorly supplied in this respect, for the developable water powers of these two districts are only 84,000 and 27,000 h.p. respectively. The middle-western states of the United States have a rather similar condition to deal with. And so it is with many of the water powers of other portions of the world. Therefore the figures given above for the world supply of water powers must be reduced greatly, *possibly to less than half* if the economic possibility of the use of a given fall is to be taken into account. But in the future, when coal becomes more and more expensive, as this fuel gives out, and the best coal-layers and those most easily worked fail, then greater and greater exploitation of the water powers will be a necessary economic result.

One undesirable feature of water powers is that they only occur in certain definite places which Nature has determined for us, while steam power can be used nearly where we wish it, and is especially useful in those districts which lie along lanes of water-communication, i.e. navigable rivers and canals where the cost of transportation is lowest, and where the industries tend to gather. This difficulty is far greater for example in Sweden than in Norway, for in the latter country, because of the deep and long fiords running far into the land, the most powerful water-falls generally lie near the coast. In order to use the power of a water-fall in places not immediately adjacent to the fall, the power must be converted into electric energy, so that it can be transported by electrical conductors. But such transportation is itself quite expensive, and loss of power occurs in the costly transmission lines. In spite of this

difficulty the transportation of electrical power has become so great that, although in 1897 only 4 percent of the water-powers of Sweden were changed into electric power, this had increased in 1906 to 33 percent, and in 1916 was not less than 75 percent. By far the greatest part of the water power used in the last twenty years has passed through electrical power-plants. For the electrical power has the extraordinarily great advantage over the unchanged water power and steam power that it can be distributed in practically as small quantities as is desired. This fact is what makes feasable the so-called electrification of a country. The electric power serves not only the great industries but also the little businesses which need only a small amount of power, such as a few horse power or even fractions of a horse power. From the viewpoint of social economics this fact is one of great importance, because one of the most undesirable features connected with steam-driven industries has been the necessity of centralization in enormous factories.

Important as water power may be, especially in certain portions of the globe such as North America, Scandinavia and the Alpine countries, we cannot hope that they will completely take the place of steam power, based on the burning of coal. The use of coal in the last century increased so much that now in each ten years nearly as much coal is burned as was burned in all the previous time since coal came into use. In other words the yearly consumption of coal has mounted to double in ten years. Naturally this cannot go on for any long period. Yet civilization's advance demands an increasing power supply. It is not possible that increased water power development can fill this continually growing need. There appears to be but one road out of this difficulty and that is the direct use of solar radiation, which, as has been stated above, supplies the earth annually with 110,000 times as much heat as is obtained by the burning of coal. If only a small fraction of this heat could be converted into work, then it would be possible to supply the energy-needs of the world, however large we might set this



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THE ROOSEVELT DAM IN ARIZONA.

In its particular location this dam is of greater service to man in holding a water reserve used mainly for irrigation rather than for power. Similar projects such as the Elephant Butte Dam furnish great water-power.

need to be. It is clear therefore that we ought to try to solve the great problem of the direct application of solar heat to the production of mechanical work.

Machines used for the conversion of solar heat in this way are called sun-engines. Since undoubtedly they will be one of the most important of the tools of man in the future, a description of such sun-engines as have so far been designed should be of interest, even though their present practical use is very slight.

The engineers of antiquity, such as Euclides and Archimedes, and especially Hiero of Alexandria discussed in their writing the possibility of using solar heat as a source of power. The first attempt to build such a machine, deriving power from the sun's heat was that of Mouchat, who constructed such a machine in Algiers in 1860. This was of very simple construction, for it was a large copper funnel, silvered on the inside. When the axis of the funnel was turned in the direction of the sun the rays of sunlight which fell on the inner wall of the funnel were reflected against the axis. This consisted of a little blackened cylindrical steam boiler, which was thus heated. It gave 3.1 kilos of steam at atmospheric pressure in each hour and furnished one-ninth of a horse power. It was calculated that the total power of the rays falling into the funnel opening of 2.2 meters diameter was about 3.6 h.p. so the efficiency of the machine was about 3%. Steam engines of that day were only 6% efficient, and this figure was even less with smaller engines. Today steam engines can give three times better results, so perhaps the efficiency of such a solar engine might be greater under modern conditions.

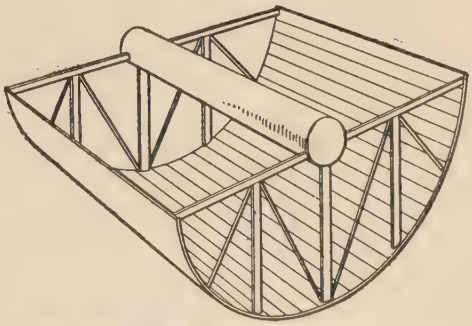

FIG. 18. JOHN ERICSSON'S SOLAR-ENGINE.

John Ericsson improved this machine by replacing the costly reflecting funnel with a collection of small ribs of glass, silvered on the back, this coating varnished. These ribs were mounted in an iron frame so that they formed a curved surface of parabolic cross section and in the focus of the parabola was placed a small cylindrical steam boiler of the length of the ribs (see Fig. 18). The reflector arc was mounted perpendicular to the solar radiation. John Ericsson made a study of this sort of apparatus in New York City and found that it had a power of one-tenth horse power for each square meter of mirror surface. It is of course possible that these results were especially favored by circumstances.

In more recent years an experimental station with five such mirrors of giant dimensions (60 by 4 meters) have been worked near Cairo, Egypt, with practical results. The builder was an American engineer named Shuman. The steam-pan was horizontal, as was the mirror axis. It was automatically turned so that the mirrors received the greatest possible radiation at all times of day. This plant was studied in 1913 by an authority, Ackermann. He found that its effectiveness was 60 h.p. per acre of earth-surface, over which the mirrors were mounted. The mirrors, in order not to hide one another in the morning and afternoon, must have space three times greater than their own actual open surface. Ackermann believed that the efficiency of these engines could easily be raised to 50%. In this event, and with the cost of construction and operation counted in, a horse power hour would cost about 20¢ and if the energy was changed to electric power this, in Cairo, should cost about $3\frac{1}{2}$¢ per kilowatt hr. This is a very moderate price. In Stockholm just before the war the price of lighting current was 8¢ and power current 4¢.

Of course it is apparent that sun-machines with a horizontal axis cannot be used except in the tropics. In Cairo which lies on the thirtieth parallel of north latitude there is lost by the angle of fall of the radiation against the mirrors about 13 percent of the energy, and this loss would rapidly increase as one

passed from the equator. At 40 degrees of latitude, (Boston and Rome are at 42°), the loss is 23 percent. The practical reason for a horizontal construction of such machines is the inexpensiveness of this construction which more than overbalances the loss of 13% in solar radiation, or in other words the necessity of increasing the mirror-surface by 13%.

The portion of the earth's surface lying between 30 degrees north and south latitudes make up half of the whole earth-surface, and quite a large part of this same area is made up of wastes and deserts where the sun shines almost continually throughout the day. So space for the use of solar engines is not lacking.

Another source of power, which has been in use for a long time is the wind. It is used generally through the device of the wind mill. In Amcrica, wind motors are quite common, especially in agricultural districts. They generally have a form such that the wings lie close together and expose to the wind a circular area. This type is also widely distributed in Scandinavia. According to American data the wing surface per horse power is 76 square meters. A wind motor of American make and of 6½ meter wing length could thus raise eight horse power. Wind motors are naturally of greatest use in an area where a wind can be counted on with considerable regularity, and where it will not be over-powerful. This condition is to be found in flat lands and along coasts. In Sweden a wind of sufficient strength is blowing about one-third of the time, so wind motors stand idle twice as long as the time that they are in motion. They are used to particular advantage in Denmark for there is often a steady wind across that low country and the wind motor has thus become of considerable importance, especially since Denmark has no coal or water power. The well-known Danish physicist, Paul La Cour, has carried on many researches on this problem. He constructed mechanical devices, called cratostats, to compensate the variations in speed of the motor due to the ever varying wind power. To store the power against times of quiet air he coupled dynamos to the

axle of the driving wheel and so charged electric accumulators or decomposed water into hydrogen and oxygen, so that these could later be burned together. The contrivances are ingenious but it is doubtful if wind motors will ever be useful for large industrial powers. The cost is too great to permit them to compete with steam motors as long as the price of coal is not higher than it was before the outbreak of the war. When coal begins to disappear from the world markets, wind motors may come into use on a larger scale. Certain tracts of the earth surface may some day become of importance for the very reason that high winds prevail, in areas where solar engines could not be used to advantage.

The amount of energy to be found in the winds is unbelievably great. Svedrup has calculated that the amount of energy taken up by the wind amounts to two and a half percent of the total energy of solar radiation, or 256 times more than the solar energy used by the plant world. Also the energy of the wind is far greater than that of water-falls and indeed than any available source of energy on earth except the solar radiation, itself the ultimate source of the power of wind and water-fall.

Solar radiation brings about evaporation of water from water surfaces, from plant leaves, and from damp earth. The vapor thus formed is lifted and carried by air streams to higher air layers where it condenses to cloud and finally falls as rain. If one could make use of all the energy to be found in rain one could obtain far more work than can be obtained from water-falls. But both in rain and wind the energy is too *distributed* to permit man to gather it together without erecting establishments of an enormously extended nature. The same is also true about the solar radiation, whereas coal or water-falls supply highly *concentrated* energy, and this is the reason of their extraordinarily great value and usefulness.

The value of water power is lessened, as stated above, by its variability with the seasons. This is particularly true of mountain torrents whose volume of water is greatly reduced in the winter time, when snow precipitates instead of rain, and

then with the melting of the snows a spring flood occurs. In the north the condition of high water may extend well into the summer. The amount of water may change from one volume to fifty volumes or more in different parts of the year. Lakes, which are common in the courses of streams, act to equalize the waterflow and it is often economically feasible to dam up artificial lakes for the storage of energy. To care for the periods of low water, reserve-units of steam power are often provided which will keep the factories running in the periods of weak or failing water supply. This naturally makes for greater cost of installation. On the other hand during the period of high water extra power can be obtained and certain chemical factories make use of this; plants which need much power and can work for a short season. Of course storage batteries can be placed in the power plant for storage of electric energy to equalize the varying and uncontrollable waterflow during different parts of the day, but not over long periods.

In the solar engine the available energy increases from zero at night to a maximal value in the middle of the day. Power which can be supplied constantly through a six or eight hour day is necessary for a factory keeping such hours. Such sun-power is not directly useful for the purpose of illumination for it would be needed during just the hours of darkness in which the supply would fail, so that it would have to be stored up in accumulators. In tropical regions the differences in solar radiation at different times in the year are negligibly small and in deserts the population density would be low, so here solar-engines should be of epoch-making importance. One can imagine how, by the use of solar machines great areas of land could be artificially irrigated so that they would be changed from desert land into fruitful crop-bearing country. Also one could make ice with the solar machines to mitigate the conditions of existence in such regions.

One great problem is that of cheap and efficient storage devices. The energy supplied by nature is supplied in enor-

mous excess of our needs. The problem is to collect such energy and to store it from the time of excess for use in the time of want. Probably the spirit of discovery will some day celebrate great triumphs along this line, and contribute highly to the progress of mankind.

Chapter X

ELECTRICITY AND CHEMISTRY

In the 18th century considerable interest was turned to the large static electric machines in which electricity was obtained by rubbing glass against cushion-like rubbing cloths. People particularly concerned themselves with the effects of the discharge upon the human body. But they also studied the action of the discharge upon the most varied then known substances and they obtained some very interesting results. Thus Beccaria found that metal oxides could be reduced to the metals by the action of this electric discharge; zinc and mercury were freed in this way from their oxides. Van Marum found that the opposite action, that of oxidation of a metal such as lead, could be produced, if the oxygen of the air was not excluded. His experiments paved the way for the researches of the famous scientist, Joseph Priestley, who studied the action of electricity upon liquids such as water and alcohol, resulting in the formation of hydrogen. In this manner Deimann and Paets van Troostwyk in the year 1789 decomposed water into hydrogen and oxygen. The most interesting phenomenon of all was observed by the German, Ritter, in 1801. He led a current from an electric machine by means of poles of silver wire through a solution of a silver salt and he found that silver passed from the positive pole to the negative pole, that is to say, in the direction of the current.

One year previously the famous investigator, Volta, had made the discovery of the epoch — the voltaic pile or battery. With its aid much greater quantities of electricity could be gained than from the old electric machines, which gave only a small current of much higher voltage than the voltaic pile, so the latter did not give such long sparks as did the

electric machine. In chemical activity however the static machines did not come up to the voltaic pile. This latter became a highly prized instrument in laboratories of chemistry and physics. In 1800 two Englishmen, Nicholson and Carlisle, decomposed water by the use of the voltaic pile. In the next year Davy began his useful experiments with the pile, leading to the discovery of the metals potassium and sodium, and in 1808 to the preparation of the elements calcium, barium, strontium, magnesium, and boron. Similar researches had been begun in 1802 by Berzelius, the famous Swedish chemist, and these gave him the material for the development of his electrochemical theory which long prevailed in the scientific world. In 1801 Volta devised the so-called table of electro-motive force of the metals, setting these in the following order: zinc, lead, tin, iron, copper, silver. If two of these metals were brought into contact with one another, then the metal first named in the table became positively charged, the other negatively charged. Ritter (in 1801) noted that the metals would throw each other out of solution in the same order. Thus zinc throws out lead from a lead solution, lead throws out tin, etc. Zinc can throw out all the five following metals from solutions of their salts; lead only the four following it, etc. Ritter concluded it to be probable that this ability of metals to act on one another was connected in some way with their electrical properties. So it could be considered that zinc was more positive, in a chemical sense, than lead, and that zinc was the most positive and silver the most negative of the six metals named above.

An important addition to electrochemical theory was made by Faraday in 1834. He showed that in electrochemical decomposition (electrolysis) the same amount of electricity always set free from different compounds a so-called chemically equivalent amount of the substances which were contained in the solutions undergoing electrolysis. By an " equivalent amount " the chemist understands the amount of a substance which can replace another in chemical compounds.

From the law of Faraday it can be concluded that chemically equivalent amounts of substances are always accompanied by one and the same amount of electricity.

An explanation of this fact first came in 1887 in the theory of electrolytic dissociation [which was set forth by Prof. Arrhenius–Tr]. According to this theory the substances to be found in solution which can be transported by the current are partly decomposed into positively and negatively charged particles. These particles are called "ions." If an electric current passes through a salt solution the negatively charged ions move toward the positive pole and the positively charged ions move toward the negative pole. The substances which, when dissolved in water conduct electricity, i.e. fall apart or "dissociate" into positive and negative ions, are called by the chemists "salts," or "electrolytes." Acids and bases belong to this category and an acid may be defined as a salt whose positive constituent is hydrogen. A base is a salt whose negative constituent is the combination OH, one atom of oxygen bound to one atom of hydrogen, called "hydroxyl." Water, therefore, which is made up of one positively charged hydrogen ion and one negatively charged hydroxyl ion, plays, from an electro-chemical viewpoint, the role of both an acid and a base. Such substances are called "amphoteric" electrolytes. To this type belong the proteins — substances of great importance in living nature. The theory of electrolytic dissociation has been the foundation for all modern electro-chemistry.

The greatest of the difficulties which this theory has had to overcome can best be explained by an example: If we take one gram of sodium chloride dissolved in 100 grams of water, the majority of the salt — about 81%, is supposed to exist in the solution according to the theory in the form of the individual constituents, positively charged sodium and negatively charged chlorine. But every chemist since Davy's day has known sodium as a very soft metal which floats on water and dissolves in the water with rapid decomposition of the latter. He knows that in such decompositon hydrogen atoms are freed

from the water, and that pairs of these atoms combine to form hydrogen gas, H_2, and bubble out into the air, while the sodium combines with the hydroxyl thus set free to form sodium hydrate, NaOH. Chlorine is known to the chemist as a greenish-yellow, evil-odored gas, which when it dissolves in water lends to the solution its properties of odor and taste. How then can one claim that this one percent solution of common salt contains a mixture of these two substances? It becomes necessary to postulate that the chlorine in common salt is not ordinary chlorine, but is chlorine carrying a charge of electricity, and that the sodium is not ordinary sodium, but carries a positive charge. Opponents have said that it cannot be that such a slight difference can bring about so great a change in the properties of sodium and chlorine. Recent researches into atomic structure resulting from the discovery of radio-active phenomena have shown us that the chemical properties of atoms depend completely on their electrical charges and, according to our present knowledge it is clear that the ion, chlorine, is something quite different from neutral chlorine, for the former possesses an electric charge which is absent from the latter. Modern electrical theory tells us that electricity itself is made up of unit charges, just as matter is made up of atoms. The smallest particle of negative electricity is the "electron." Thus the ion, sodium, is made up of an atom of sodium from which an electron has broken off (so that it has become more positive by one unit). The ion chlorine, is made up of an atom of chlorine to which an electron has attached itself (so it has become more negative). The splendid advances which the introduction of the ion theory brought about were due in part to the fact that this theory furnished a simple explanation for the various reactions of analytical chemistry, which makes up the ABC of the chemist.

We might take for study a characteristic reaction such as the determination of silver or of chlorine. If a solution of a chloride such as sodium chloride or any salt of which one ion is the chlorine ion, is added to a solution of a silver salt, such as sil-

ver nitrate, a white flocculent precipitate results, and this looks somewhat like the precipitate which is produced in milk by rennet. At first it was stated that this reaction was characteristic for silver and for chlorine. But this is not correct since a solution of the salt, potassium chlorate, of formula $KClO_3$, does not give any curdy precipitate with silver nitrate solution, yet chlorine is one of the important constituents, as the formula shows. The ions of potassium chlorate are the potassium ion, K, and the chlorate ion, ClO_3. In general the ions of a salt are its metallic portion (the positively charged portion) and a negative remainder. So the reaction with silver above described is characteristic not for chlorine, but for the chlorine ion. Many so-called organic compounds show no chlorine ion reaction although they contain chlorine. Today the reason is clear to us, but formerly it was unexplainable. For a second example, this time of a positively charged ion we might take the ferri-ion which is to be found in solutions of ferric salts. With a solution of yellow potassium ferrocyanide this gives a characteristic deep blue precipitate called Berlin blue. This reaction is not given however by all iron compounds. The potassium ferrocyanide itself contains iron, as its name indicates ("ferrum" is Latin for *iron*) and naturally a portion of this ferrocyanide solution when mixed with another portion of the same does not give Berlin blue. Moreover there exist many different iron compounds, ferrous salts, nitroprussides, ferricyanide compounds and organic compounds containing iron, which do not give the Berlin blue reaction with ferrocyanide salts. Ferrous salts for instance give a white precipitate and this in the air or in liquids containing oxygen may quickly oxidize giving ferric ions and will then take on the blue color.

The fact is that these reactions are definite for definite ions. Since salts in solution dissociate into their ions, naturally all those which form the same ion give the same reaction specific for that ion. If the ion is not present the reaction cannot occur. This simple explanation has brought order and science

into the field of analytical chemistry. A long-awaited need was filled by the dissociation theory, and it has gained rapid recognition.

The actual motion or "wandering" of ions can be demonstrated by experiment, if one prepares a solution of one percent of sodium chloride and 4% gelatin in water and to this add a few drops of litmus solution. Litmus is a dyestuff obtained from a certain marine alga. In neutral condition it is wine red. It is turned blue by bases and turned a weak, salmon color by acids. The gelatin solution is used to fill a glass tube *ab* arranged as shown in figure 19. The tube is filled nearly to the top of its two beaker-like mouths *c* and *d* and then is let stand until the content solidifies or gels. This quickly occurs at room temperature. Then one pours into *c* a weak solution of sodium hydroxide, which is basic and contains hydroxyl ions, and in *d* one places dilute hydrochloric acid, which contains hydrogen ions and is therefore acidic. The negative pole of a galvanic battery is dipped into *c* and the positive pole into *d*. When a current is passed the positive ions are driven in the direction away from the positive and toward the negative pole. The hydrogen ions are driven into the tube *ab* at *b*, and the presence of an acid makes the litmus become colored salmon-pink at *b*, then the boundary between the original wine-red color and this new color moves further and further from *b* toward *a* the longer the experiment is continued. In the same way the negatively charged ion, hydroxyl, moves from the beaker *c*, against the current toward *a* and in the course of the reaction progresses further and further toward *b*. Its motion is made evident as an alkaline reaction which turns the dyestuff blue. In this test it can be seen that the hydrogen ions move quite a little faster (about 1.81 times more rapidly than the hydroxyl ions). These values can be determined by measuring the

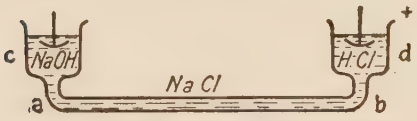

FIG. 19. APPARATUS FOR DEMONSTRATING THE MIGRATION OF IONS.

length of the areas that are salmon-pink and blue in the column and comparing them.

Investigations of the relative "speed of transport" of the ions have been very important in electrochemistry. Hittorf worked in this field in the period between 1850 and 1859. The displacement of the ions was determined by chemical analysis of the electrolyzed salt solutions to be found in the anode space (around the positive pole) and in the cathode space (around the negative pole, the cathode). The composition of the solution before the action of the current, that is to say before the electrolysis, was known and the time that the current acted was noted. Thus Hittorf could determine what substances and how much of each were transported to the anode space in each second. In the same way he determined the changes taking place at the cathode. These two analyses checked each other, for the total composition of the liquid must remain the same after as before the electrolysis. Naturally care had to be taken to count in any gases developed in the electrolysis; this was easily done by the introduction of a voltameter into the electric circuit. The current passing during the electrolysis, measured by this instrument, permitted calculation from Faraday's law of the amount of gas given off at the poles. Oxygen is commonly given off at the anode and hydrogen at the cathode. The following values for the speed of the commoner ions at 18° C. were obtained:

H	315	$\frac{1}{2}$Ba	55	OH	174	$\frac{1}{2}SO_4$	68
K	64.6	$\frac{1}{2}$Ca	51	Cl	65.5	$\frac{1}{2}C_2O_4$	63
Na	43.5	$\frac{1}{2}$Mg	45	F	46.6		
Li	33.4	$\frac{1}{2}$Zn	46	NO_3	61.7		
NH_4	64	$\frac{1}{2}$Cu	46	ClO_3	55		
Ag	54.3	$\frac{1}{2}$Pb	61	$C_2H_3O_2$	35		

From these figures the conductivity of salt solutions can be calculated. They are the so-called equivalent conductivities at eighteen degrees C. of the ions named. By the equivalent conductivity of a solution we understand its specific conductivity

divided by its concentration given in gram equivalents per cubic centimeter. In other words the specific conductivity can be obtained by multiplying the equivalent conductivity by the concentration in gram equivalents per cc. However these figures are only correct and useful for dilute solutions, while for more concentrated solutions one must multiply by a factor, always less than one, which corresponds to the degree of dissociation, and which is indicated below by "L." This matter can be explained better with an example. Suppose we wish to determine the specific conductance at 18° of a one percent solution of sodium chloride, or, better stated, a solution containing one gram of sodium chloride per one hundred cc. of water. The equivalent weight of sodium chloride, NaCl, is: $23 + 35.5 = 58.5$. So the concentration of the solution, in gram molecules per cc. is $1/58.5 \times 1/100 = 0.000171$ and the specific conductance $K = 0.00171\ (43.5 + 65.5) \times L$ —— (L here is 0.81).

Certain definite rules govern the degree of dissociation. The table given below supplies the values of this for three salts, KCl, K_2SO_4 and $MgSO_4$ in solutions of normality n. A normal solution of the KCl contains 74.6 g. per liter (K = 39.1, Cl = 35.5 so KCl = 74.6). The value for $\frac{1}{2}$ K_2SO_4 is 87.1 gms. (2 K = 78.2, S = 32, O_4 = 64 so K_2SO_4 = 174.2 and the equivalent weight, $\frac{1}{2}$ K_2SO_4 = 87.1). The value for $\frac{1}{2}$ $MgSO_4$ is 60.2. A solution of normality n holds n times as much of the given salt per liter.

n	KCl	K_2SO_4	$MgSO_4$
0.01	94.1	87.0	67.8
0.1	86.0	71.0	44.3
0.5	78.7	58.3	31.3
1.	75.6	53.2	25.6
2.	71.2	—	18.9

Values almost the same as those found for KCl serve also for other salts that are composed of two monovalent ions, such as NaCl, KNO_3, potassium acetate, etc. These figures also hold very closely for acids made up of two simple ions such as HCl, HBr, etc. and for KOH, NaOH, etc. The latter salts

actually conduct electricity a little poorer than according to the figures of the table. Thus the figure for 0.1 n NaCl is 84.4, while for 1 n NaCl it is 68.3. This is probably dependent on the fact that these salt solutions are a little more viscous than is the KCl solution, and this deviation increases with increasing concentration. In practically a similar manner the K_2SO_4 divides up into two simple and one divalent ions K-K-SO_4, as do many other salts such as sodium sulfate Na_2SO_4, calcium chloride, $CaCl_2$, while salts with two divalent ions such as $CuSO_4$ and $ZnSO_4$, behave very like magnesium sulfate in their dissociation. All these figures are for a temperature of 18°C.

The speed of the ions increases greatly with the temperature for each degree: the H ion, 1.5%, hydroxyl, 1.8%, other monovalent ions 2.3–2.5%, if the value at 18°C. is taken as unity. The degree of dissociation decreases very slightly as the temperature rises. By the aid of the figures the conductivity of salt at ordinary temperatures can be calculated quite closely, and this is of great practical use. It is simplest to calculate the conductivity at 18°C. and then to add about 2.2% for each degree of temperature above 18° C. At temperatures below 18° one subtracts the 2.2% for each degree. In the case of sulfuric acid solution the correction for each degree is about 1.3% and in the case of monovalent acids such as hydrochloric and nitric acids is about 1.5%, for potassium hydroxide it is 1.9%.

Weak electrolytes such as the weak acids, for example acetic acid, or weak bases such as ammonia, follow much more closely the theoretical conditions than do strong electrolytes. For the weak salts the law of mass action of Guldberg and Waage holds true (see page 195). Ostwald was the first investigator to note this fact, and thus to furnish support to the dissociation theory. When not too greatly diluted these solutions of weak acids and bases increase in their conductivity in proportion to the square root of their concentration, so the specific conductivity of an acetic acid solution decreases to half-value if its volume is increased four times by dilution. We must assume

here that the temperature remains unchanged, for the conductivity of these acids and bases, like that of the strong acids and bases increases with increasing temperature.

Explanation of why the strong electrolytes do not follow Guldberg and Waage's law has been a difficult matter. Many investigations have shown that these do follow the law when in extremely great dilution, at concentrations below one five-hundredth normal. For practical purposes this regularity at great dilution is of little use, but it is of the highest interest theoretically. The deviation from the law in higher concentrations appears to be dependent on an increase in dissociation due to an action of the salt upon its own molecules.

Volta built his first galvanic cell or battery from zinc and copper plates dipped in sulfuric acid. In modern batteries the copper plate, which was found to be rapidly attacked chemically, is replaced by a carbon plate. It was soon evident that these carbon-electrode cells very rapidly lost their power because current passing through them covered the carbon plate with a layer of hydrogen (a process called polarization). By the addition of an oxidizing agent to the sulfuric acid this difficulty could be more or less overcome. Thus for example in Grenet's cell, potassium bichromate or chromic acid is added. In Bunsen's cell nitric acid is used, contained in a porous cup into which the carbon electrode dips. In the Lechanché cell, much used for bell-ringing and for private telephone installations, the oxidation agent is manganese dioxide packed about the carbon. In this cell which furnishes an electromotive force of 1.6 volts, there is used in place of sulfuric acid a solution of sal ammoniac in water. This is able like sulfuric acid to dissolve the zinc oxide which is formed on the zinc electrode by the action of the electric current. In this cell the power decreases during use, but increases again on standing. So such a battery will not serve for continuous use. It has been found desirable moreover to amalgamate the zinc — i.e. to coat it with mercury which latter combines with the zinc and prevents too rapid attack by the electrolyte.

The simplest of the so-called non-polarizing cells is the Daniell cell (Fig. 20) which has been much used in telegraphy. It consists of a zinc rod dipped in a porous cup filled with zinc sulfate solution. The cup is placed in a glass cylinder filled with copper sulfate solution and is surrounded by a cylindrical plate of copper. This copper plate has a slit to facilitate the circulation of the copper sulfate solution. Beside the zinc sulfate, sulfuric acid is generally poured into the porous cup to increase slightly the electro-motive force of the cell and to decrease resistance. A modification of this cell by Meidinger has the advantage that it does not require the porous cup. The two liquids are kept apart by the differences of their specific gravity only. The copper plate lies at the bottom of a glass jar and a copper wire insulated with gutta-percha is led from this to the top. The copper plate is covered with a saturated solution of copper sulfate, and to keep it in saturated condition a smaller glass cylinder filled with copper sulfate crystals and water, is placed in the vessel. Over the copper sulfate solution a solution of magnesium sulfate is layered in, and in this is hung an amalgamated zinc electrode. In Callaud's cell the copper plate is embedded in copper sulfate crystals and a zinc sulfate solution is used instead of a magnesium sulfate solution. In these Daniell type batteries the zinc dissolves during the passage of the current and an equivalent amount of copper is plated out on the copper electrode.

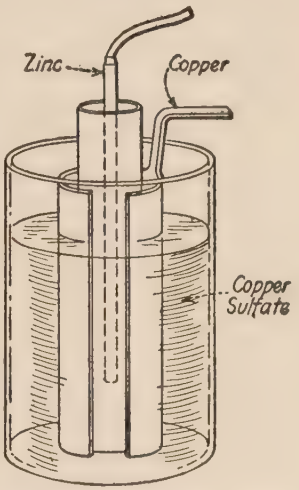

FIG. 20. THE DANIELL CELL.

A cell of a very simple type is the Cupron cell, which consists of electrodes of zinc and copper, the latter covered with a thin layer of its oxide. Both are dipped into a 30–40% po-

tassium hydroxide solution. When the cell delivers current the zinc dissolves in the alkali, while an equivalent amount of copper is reduced from oxide to metal and one equivalent of water forms. This cell is notable in only containing one fluid, and so needs no diaphragm, also it does not deteriorate to any extent with use, for the copper oxide is but very slightly soluble in the potassium hydroxide. Furthermore, and this constitutes the greatest advantage of the cell, it can easily be renewed when the copper oxide is used up, by leaving the plate of copper for some time in a hot place such as an oven, whereupon it becomes again coated with oxide from the oxidizing effect of the air.

However all such elements have been largely replaced in recent years by storage batteries, the first of which was made in 1860 by Gaston Planté. It consisted of two lead plates dipped in 15–20% sulfuric acid solution. If a current is led through such a cell, with the two plates serving as the poles, hydrogen develops on one of these poles and passes off, on the other plate oxygen forms and this oxidizes the lead to lead super-oxide. If one leads the current through it in the opposite direction the lead super-oxide is reduced for the most part to lead oxide, and then this combines with the sulfuric acid to form lead sulfate and from this finally metallic lead is again formed as a soft slime, lead-slime. By reversing the current many times the plates are softened in a deeper and deeper layer and changed to the lead-slime and the lead super-oxide. This process is called "forming" the plates. To aid this process the plates are scored and also punctured and then filled with lead oxide or red lead, and sulfuric acid, forming a sort of cement. The sulfuric acid used in the storage cell must be free from impurities, chlorides, nitrates or from other metals than lead, copper being especially undesirable, for these impurities tend to destroy the plates. At the end of the charge there is forming on the lead super-oxide plate, hypersulfuric acid, which decomposes to sulfuric acid and oxygen. The latter then develops as a gas. It is then said that the stor-

age battery is gassing, and it is a sign that it is fully charged. At the same time hydrogen develops at the plate of lead-slime. If use is now made of the storage battery, i.e. if a current is taken from it, first the small remainders of hypersulfuric acid and of hydrogen at the plates are used up, then the electromotive force becomes practically constant at about 2 volts and the principal process begins. The lead super-oxide, PbO_2, and the lead mud react with sulfuric acid to give lead sulfate and water according to the chemical equation:

$$PbO_2 + Pb + 2\ H_2SO_4 = 2\ PbSO_4 + 2\ H_2O\ (+ 43500\ \text{Cal.}).$$

At first the electromotive force decreases very slowly, then faster to about 1.9 volts. The cell can be worked a little longer, but it is not best to let it go below 1.8 volts. It is then said that the storage battery is discharged. It cannot be left any long time in this condition, for the lead sulfate would crystallize out and then its re-solution would be difficult. Even if the battery is fully charged, if it is allowed to stand it loses part of its charge and deteriorates.

Among the undesirable features of the lead storage battery may be counted the softness and the weight of the lead. Because of the softness of the metal thin lead plates cannot be used, for they might buckle, so quite thick material must be employed and this increases the weight. This factor of weight hinders the use of storage batteries for many purposes, for example for driving motor vehicles. Many researches have been made to make storage batteries out of other metals than lead. There has been a certain degree of success in adding a little antimony to the lead ("Julien" metal with about 4% antimony) so that the lead is hardened. A storage battery using another metal was discovered by Jungner and has received industrial development by Edison. One pole is made of an iron plate, impregnated with ferrous oxide and graphite. The other is a nickel plate impregnated with nickelous oxy-hydrate. On charging this battery the ferrous oxide is reduced to a finely divided iron slime and the nickelous oxy-hydrate becomes

oxidized to nickelic-oxy-hydrate. The electrolyte is potassium or sodium hydrate. The electromotive force is 1.3 volts.

All the various commercial types of galvanic elements change more or less rapidly in the electromotive force they can supply; the storage batteries are the most constant in this respect. For making measurements of electromotive force it is necessary to make use of a cell with an electromotive force as nearly as possible to unchanging. The Daniell cell above described was once used for this purpose, when filled with a sulfuric acid of specific gravity 1.075 and a copper sulfate solution of specific gravity 1.195 at 18° C. The electromotive force of this cell is 1.176 $[1 + 0.0002\ (t-18°)]$ volts, where t is the temperature in centigrade degrees. This "normal Daniell cell" as it is called displays one difficulty, the copper sulfate diffuses gradually into contact with the zinc and copper precipitates, so that the cell deteriorates. Therefore it has to be freshly arranged every time it is to be used. The type of Daniell cell using zinc sulfate has a low electromotive force, about 1.096 volts, and displays the same undesirable feature.

The only metal which will not injure the amalgamated zinc electrode of a cell is mercury. So this has been used in the manufacture of normal cells whose electromotive force can continue unchanged over a long period of time. The first such cell was made by Helmholtz. The zinc pole was surrounded by a 10% zinc chloride solution. The other pole consisted of a layer of mercury covered with calomel and 10% zinc chloride solution. The electromotive force of this cell is 1.074 $[1 + 0.001\ (t-20°)]$ volts. Here too there is a difficulty — the concentration of the zinc chloride solution changes by evaporation.

In the Clarke cell therefore it is replaced by a saturated solution of zinc sulfate, and this does not change as long as the temperature remains constant. One pole of this cell is a zinc amalgam of 10% zinc and 90% mercury, covered by crystals of zinc sulfate. The other pole is pure mercury covered with crystals of mercuric sulfate, and above that with zinc sulfate. Between the two poles there is placed a solution of zinc

sulfate which is kept saturated by the presence of the zinc sulfate crystals. The electromotive force is 1.433 [1 − 0.0084(t−15°)] volts.

The zinc and zinc sulfate of the Clarke cell have since been replaced by Weston with cadmium and cadmium sulfate, in the solution and in solid form. The electromotive force of the Weston cell is 1.019 [1 + 0.0004 (t−20°)] volts. It is notable for the slight variation with temperature (only 4/1000ths per cent for each degree). The electromotive force is but 1.9% higher than one volt, making calculation of the results of measurements with these cells simple. The normal cell with a mercury electrode can furnish no powerful current without rapid deterioration. It has to be carefully guarded in using it for measurement. The Helmholtz cell is injured least in this way.

By the use of galvanic cells work can be done, for example motors can be driven. The energy available depends on the type of cell used, for example in a Daniell cell the necessary energy is dependent on the precipitation of copper from copper sulfate solution by zinc. For one equivalent of copper, 31.7 gms. (half the atomic weight), 32.7 gms. (half the atomic weight) of zinc must be used. If this process goes on by itself, that is to say if one places the stated amount of zinc in a solution of copper sulfate 25,055 calories of heat are developed. So it would appear probable that the amount of electric work obtainable from this reaction going on in a battery should be equivalent to this amount of heat. Using this observation Helmholtz in 1848 calculated the electromotive force of a Daniell cell. According to his figures one obtained the electromotive force in volts if one divided the amount of heat in question by the factor 23,070. This gives a result for this cell of 1.088 volts, whereas the determined value is 1.096 volts. Similarly for the lead storage cell the calculated figure is 43,500/23,070 = 1.886 volts, while the determined value is 1.9 and 2 volts. It was later discovered that the higher actual value depended on the use in the lead storage cell of

a more concentrated sulfuric acid than had been used by Thomsen in his determination of the heat that develops during the change of lead and lead oxide into lead sulfate. The agreement is generally satisfactory. But the rule does not hold for all cases. In another series of researches Helmholtz found that his values only gave correct results in certain cells which do not change their electromotive force with temperature. It came very close to correct for the Daniell cell and the lead storage battery. In other cases the agreement was not so good. He then determined the proper correction for temperature change, and the calculations when thus corrected were in good agreement with the experimental results.

At first the Bunsen cell with nitric acid was much used. It had the disadvantage that it gave off vapors dangerous to the health. It has been supplanted almost wholly by the lead storage battery, charged by the aid of a dynamo. In making the charge one uses a certain amount of energy, while in the discharge one gets a certain proportion of this back. The remainder is lost, and more is lost in a rapid than in a slow discharge of the cell. With a time of discharge of 10 to 12 hours the working efficiency is 83%, that is to say 17% of the energy is lost. One may ask why we do not directly make use of the energy instead of leading it into a storage battery? This is because of the great irregularity with which the electricity must be used. Most factories are shut down during the greater part of the night, electric illumination is slight, often the street railways do not run, so the power obtained at the electric plant is used in charging batteries in order to save it for the daytime when at certain hours the power-need may sharply rise. The number of dynamos in use can of course be changed, but with steam power it is not advisable to shut down completely; the fires must be kept beneath the boilers. With water powers a certain amount of damming back of the waters may be possible in the hours of light-load.

Electrochemical processes are used considerably in industry.

The oldest such process is galvanic gold, silver and nickel-plating. Objects to be covered with these metals are hung in a bath composed of a solution of a salt of the metal in question commonly in the case of the rare metals a double-salt with potassium cyanide, and then the current is passed through so that the gold or silver or nickel are precipitated on the object, which, if it is not itself metallic, is made a conductor of current by means of a coating of graphite. For nickel-plating nickel sulfate is ordinarily used in a dilute citric acid solution. Copper and iron can be precipitated in the same way. Copper tubes or pipe have been made by precipitating copper by electrolysis on rotating cylinders; such tubes are better than those made by brazing. Brass tubes are also made in this electrical way.

Galvano-plastics are objects made by precipitating a copper coat on a "negative" of pressed or moulded wax or gutta-percha, made to conduct the current by a coating of graphite. These thin forms are backed with type-metal to make them more solid and less fragile. Electrotypes are made in this way and photo-engraving work is thus done. The master records for the preparation of phonograph records are thus copied from the original, wax, recording disks.

Of especial importance are the electrolytic methods for the separation or refining of metals. These have come into use since the electric current has become cheap. We have mentioned above that this method is used for the refining of copper. The raw material is hung in the bath as an anode and is brought into solution by the passage of the electric current and carried to the cathode, (a plate of thin copper), where a very pure quality of copper again deposits. The tiny amounts of more valuable metals contained in the raw copper, as well as various other impurities, remain undissolved and sink to the bottom of the bath as an anode — mud or slime. This mud is of great value, and is worked up for its various constituents. The pure copper precipitated on the cathode is of much greater industrial value than the impure copper, particularly because

of its higher electrical conductivity. It is used in electrical machinery and conducting wires (see p. 77).

Electrolysis is used as a method of preparation of caustic soda from sodium chloride. The sodium out of the sodium chloride precipitates on the cathode as metal, but the water of the solution immediately decomposes it to sodium hydroxide and hydrogen. At the anode there is developed chlorine gas which can be made into chloride of lime, the well known bleach and disinfectant. In making these products the liquids at the anode and the cathode must be separated by a diaphragm to hinder mixing. If this is not done the sodium hydroxide mixes with the chlorine and there is formed sodium hypochlorite, or bleaching liquor, used for a bleach in many industries and especially in wood-pulp factories. Caustic soda and chloride of lime are also very valuable in such factories. Chlorine also is useful for the manufacture of bromine, and in the dye industry for such purposes as the manufacture of artificial indigo. Hydrogen gas (formed at the anode) is used to some extent for filling balloons and for obtaining a high heat by means of the blow-pipe flame and is of great use in the arts today in the manufacture of ammonia by the fixation of atmospheric nitrogen in Haber's process. Electrolytic methods for the preparation of caustic soda have practically completely replaced the old method of caustification with slaked lime. The caustic soda is a necessary chemical in many processes of which soap manufacture is the most important. In this latter technique the soda lye is allowed to act on fats, and a soap is formed, together with glycerine. If potash lye is used in place of soda a soft soap results.

Caustic potash is made by electrolyzing the potassium chloride found in the Stassfurt and Alsatian salt deposits, in the same way that caustic soda is made from sodium chloride. From potassium chloride in alkaline solution electrolytic potassium chlorate is made, much used in the igniter material of matches, and prepared in large quantities. The electrolytic preparation of the light metals is of great importance; potas-

sium, calcium, magnesium and particularly sodium and aluminium, of great use in the arts, are made in this way.

Next after the first preparation of alkali metals by the electric current, the use of that current as a source of light was an event that awakened interest. The arc-light was discovered by Davy in 1813 and was long called Davy's arc. The first electric light was obtained by the use of galvanic batteries, especially of Bunsen cells, until the discovery of the dynamo made it cheaper and easier to prepare electricity with its aid. The temperature prevailing in the arc light is around 3500°C. and processes can take place in this high temperature which were not possible at the temperatures available up to the time of discovery of the arc. High temperatures can also be obtained by heating carbon with the electric current, and such a method is used a great deal nowadays for the preparation of many useful substances such as the grinding material, carborundum, a silicon carbide, SiC_2, which was discovered by the American, Acheson in 1891. It is made from coke and silica-sand in the presence of a little common salt, and the electric current is led through the mass by means of a core of granular coke.

A further important product of such electric furnaces is calcium carbide, (CaC_2), obtained by heating a mixture of lime and carbon to 2000° by means of the electric current. If nitrogen is led over the calcium carbide at a high temperature there is obtained a valuable fertilizer material, calcium cyanamide, $CaCN_2$. Also artificial graphite, even better in quality than the natural product can be made in similar manner to the carborundum by heating carbon alone, unmixed with sand, but with a bit of iron oxide, alumina or silica added. Alloys of aluminium with iron or copper are made in the electric furnace from a mixture of bauxite and carbon with iron or copper scrap. In recent years there has come the development of electric steel furnaces, and even of electric blast-furnaces for the smelting of iron direct from its ores. Electrical methods of heating have many advantages over ordinary methods. The

heat can be localized and thus the losses of energy can be lessened and very high temperatures obtained. By regulating the current the temperature can be controlled at all stages of the process in question.

The introduction of electrical methods, both those dependent on electrolysis and those employing high temperatures, have effected great changes in the chemical industry. It is very likely that we are only on the threshold of development in these fields. Sweden, Canada and Alaska are lucky industrially in possessing comparatively immense supplies of available hydroelectric power at comparatively low cost.

Chapter XI

THE COURSE OF A CHEMICAL PROCESS

In another chapter (see p.35) we have had occasion to speak of a chemical equilibrium. Such an equilibrium occurs in the electrolytic dissociation of weak bases and acids. The acid which we call acetic acid has probably been known from early antiquity (as vinegar). At 14.1° C. in 1/1500th normal solution, which corresponds to a solution of 0.04 gms. of glacial acetic acid per liter of water, the acid has a specific conductivity of 0.0311. The equivalent conductivity is 1500 times larger, 46.6 tenths. In acetic acid, HCH_3COO, the ions are the hydrogen ion, H, present in all acids, and the acetate ion, CH_3COO. The equivalent conductivities of these two ions are 315 and 35 respectively (see p. 181), and together would make 350. The conductivity at 14.1° C. is actually a little less: 316, according to the measurements of van't Hoff. The degree of dissociation is the quotient $46.6/316 = 0.147$. In other words only 14.7% of the acetic acid molecules in this solution are transporting electricity — which means that this proportion of them have dissociated into their ions, H, and CH_3COO, while the main bulk of the acetic acid molecules (85.3) have not split up but remain of the original composition (HCH_3COO). The undissociated molecules are in an equilibrium with the two ions so that, should the solution be made more concentrated, part of the ions would be changed back to molecules, while if water were added (i.e. on dilution) a still larger number of acetic acid molecules would split up into the ions H and CH_3COO.

According to the Law of Mass Action which was put forth by Guldberg and Waage in 1867, the concentrations of the three bodies in the solution will follow the equation here given:

$$z(H) \times z(CH_3COO) = k \times z(HCH_3COO)$$

$z(H)$ is the concentration of H ions, $z(CH_3COO)$ is that of acetate ions, and $z(HCH_3COO)$ is the concentration of acetic acid molecules. k is a constant, the equilibrium constant, and depends on the dilution. From his determinations of conductivity van't Hoff calculated that this constant k at 14.1° is 0.0000178. By the use of this figure the degree of dissociation of the acetic acid solutions was calculated, and led to results comparable with those obtained directly from conductivity determinations. The agreement of the direct determination and the calculated value is extremely good. The law holds good in the region between 0.06 n and 0.00006 n, therefore over a change of concentration of 1 to 1000. At higher concentrations aberrations occur, probably due to a lessening of the fluidity of the solution. This may make the determined value of a normal solution come out about 5% smaller than the calculated value.

The Law of Guldberg and Waage gives much greater accuracy in such a case as this, i.e., in solution, than it does when it is used for the equilibrium between gases and their dissociated particles. The most interesting case of the latter type yet studied is that of the decomposition of iodine at temperatures above 700° C. According to studies of the specific gravity of iodine at various temperatures, made by the famous German chemist, Victor Meyer, and by his French colleague, Crafts in 1880, it was found that at a pressure of one-tenth of an atmosphere and at 680° C. iodine vapor is composed of molecules of the formula I_2. This was deduced with the aid of Avogadro's law, to which we shall shortly return. In other words the molecules of iodine under these conditions consist of two atoms. They correspond to a gas density which is 8.8 times greater than that of the air at the same pressure and temperature. At 1500° however the density of the vapor is only half the figure given above, only 4.4 times that of the air, which means that under the action of increased temperature the iodine molecules have split into single atoms, I. This follows the law of Avogadro, advanced in 1811, which states

that the density of the vapor of a substance is proportional to its molecular weight. The density 8.8 corresponds to a molecular weight of 254. (The mean molecular weight of air is 28.9 and $28.9 \times 8.8 = 254$). This figure is twice as large as 127, the determined atomic weight of iodine. The molecules of iodine at temperatures around 700° where the vapor density is 8.8 times that of the air are therefore twice as heavy as the atoms of iodine, so this means that one molecule at this temperature is made up of two atoms. Above 1500°, where the vapor density of the iodine is only 4.4, these molecules are completely split down into single iodine atoms.

To be exactly correct we will add that the gas density of iodine as determined by Meyer and Crafts at 1500° and 0.1 atmosphere actually was a little higher than the above value — 4.48, so really there was 2% of undecomposed iodine still present. Thus the degree of dissociation was 98%. At a pressure of 0.3 atmosphere the vapor density was still higher — 4.61, corresponding to a degree of dissociation of 93.5%, i.e. there were 6.5% of the iodine molecules still undecomposed and still corresponding to the formula I_2.

These results of Meyer and Crafts awakened great interest at the time of their publication. Chemists at that time were little inclined to believe that chemical elements in gaseous condition could exit as single atoms, but here was a proof of it. Also the vapor density of bromine, by Victor Meyer's measurements, showed that that element at high temperatures likewise partly consisted of single atoms.

Avogadro's Law had to fight many objections at first and many studies had to be made before people were sure of its fundamental nature. Acceptance of this law was really first brought about by the great advance which soon came in the field of organic chemistry, so that many substances came to be prepared which were volatile at low temperatures, and therefore lent themselves to study in this way. But various difficulties still remained to be overcome. For example the vapor pressure of ammonium chloride, NH_4Cl, was found to be

only 1.01 whereas according to Avogadro's law it should be 1.84, the density of air always being taken at unity. Similar deviations, abnormally low vapor pressures, were found about the year 1850 for four ammonium and three phosphorus compounds. Cannizzaro, an outstanding chemist and countryman of Avogadro, explained these deviations in 1857 by the fact that the vapors of these substances are partly decomposed. Thus the NH_4Cl, sal ammoniac, the scientific name of which is ammonium chloride, decomposes into hydrogen chloride, HCl, and ammonia, NH_3. An Austrian chemist, v. Pabal in the year 1862 separated these two bodies from the vapor of sal ammoniac by a process of diffusion. The French school of chemists of that day, under the leadership of Sainte-Claire Deville, men who contributed much to science and made important studies of the dissociation of chemicals, contested his results. Their criticisms were successfully overcome and from that time Avogadro's law became the cornerstone of chemical teaching.

However the measurements which had been made in the study of these phenomena were not sufficiently accurate to lead to any certain proof of the universal application of the Law of Guldberg and Waage. Fortunately from the development of the mechanical theory of heat it was possible to bring a much better proof for the equilibria of gases. In 1867 Horstmann deduced the Guldberg-Waage law from the general laws, the truth of which has never been challenged. Then in 1885 there followed van't Hoff's epoch making discovery of the usefulness of these gas laws in the study of dissolved substances. At about the same period the theory of electrolytic dissociation appeared and van't Hoff began a series of researches to see if the Guldberg and Waage law applied to this new form of dissociation. He found a complete agreement, not only for acetic acid but also for all weak acids, so it was certain that this law of mass action and equilibrium held true for these bodies in solution. Since that time Ostwald has gathered together much material about the behavior

of weak acids in relation to this law, and von Bredig has similarly studied the weak bases, whose properties obey the gas laws completely. Finally in 1913 I succeeded in determining that these same salts in extreme dilution follow the equilibrium law, and these results were confirmed in 1918 by the American, Washburn, and his pupil, Wieland.

We have stated above that the equilibrium of the dissociation of iodine vapor depends on the temperature and the gas pressure. That is a general truth. From thermodynamics van't Hoff has derived a law for the influence of temperature, and Planck one for the influence of pressure. The influence of temperature increases in proportion to the heat which a vapor absorbs in dissociating, while that of pressure increases with the volume-change that would take place in this process, if it went on at constant pressure.

Both these laws, especially that of van't Hoff, are of general importance. All bodies which absorb heat in their dissociation — (and that includes most) — dissociate more and more with increasing temperature. The simplest case is the dissociation of salts which contain either water or ammonia. These give off their crystal-water or their ammonia with increasing temperature. A law holds here that the pressure of water vapor over the salts depends only on the temperature, and not upon the amount of the evaporated water, just as does the pressure of vapor over a water surface. Debray found in 1868 that the sodium phosphate, $Na_2H\,PO_4 \cdot 12H_2O$ crystallizing with twelve molecules of water of crystallization, gave a vapor pressure of 30.2 millimeters at 31.5°, and therefore somewhat lower than the vapor pressure of water at this temperature, which is 34.33 millimeters. As water passed off this pressure remained unchanged above the phosphate until five molecules of water were removed, so that the composition of the salt became $Na_2HPO_4 \cdot 7H_2O$. At this point the pressure suddenly sank to 21.3 mm, and remained at this figure till all the water was gone. Then of course the pressure sank to zero (all this at the constant temperature of 31.5° C.). The same rule holds for

ammonia salts. Such salts containing water and ammonia can be studied at comparatively low temperatures, and thus the accuracy of the determinations can be very great.

The equilibrium laws hold good for all solid and liquid bodies which can give off gases. A practical case is that of lime-burning. Here the raw material is limestone, which gives off its carbon dioxide in the heat and becomes calcium oxide, CaO, burned lime. Even at ordinary temperatures the limestone has a definite carbon dioxide pressure, so low, however, that it gives variable measurements, and in many cases lower than the carbon dioxide pressure of the air. There is no evaporation of carbon dioxide from limestone at ordinary temperatures. Debray in 1867, was the first to study the important process of lime-burning, and later it become the subject of study of many investigators. Even at the temperature of 450° the carbon dioxide pressure over limestone is immeasurably low. At 610° it reaches 48 mm. and mounts with increasing speed as the temperature further increases until at 910° it has reached atmospheric pressure — 760 mm. One can say that at this temperature the carbon dioxide actually "boils away" from the limestone. Just as water at atmospheric pressure cannot be heated above its boiling point, 100°, for all heat added beyond this point is used for the formation of vapor, so limestone at atmospheric pressure cannot be heated above 910° C.; beyond that point all heat added is expended in driving out carbon dioxide until pure lime (CaO) remains behind, and then the temperature can rise again. Thus we see that in lime-burning the temperature of the kiln must be brought to 910° C.

Other important cases of such equilibrium are the decomposition of carbon dioxide itself into carbon monoxide and oxygen, and that of water-vapor into hydrogen and oxygen at high temperatures. Deville discovered in 1863 that water vapor partly decomposed at temperatures around 2000° C. A number of scientists studied this phenomena, especially the French chemist, Le Chatelier, the Germans, Nernst and v.

Wartenberg, besides the Dane, Bjerrum. One of Nernst's tables of the percentage degree of dissociation at atmospheric pressure is given below:

Temperature in deg. C.	CO_2	H_2O
1227	0.041	0.022
1727	1.77	0.578
2227	15.8	3.89

The influence of pressure is particularly striking in the case of these reactions. In the decomposition of two molecules of water two molecules of hydrogen and one molecule of oxygen are formed, and from two molecules of carbon dioxide two molecules of carbon monoxide and one molecule of oxygen result; therefore, according to Avogadro's law the volume in both these cases increases from two to three. At lower degrees of dissociation, according to the law of Guldberg and Waage the dissociated portion increases from 1 to 2.15 as the pressure is decreased from 1 to 0.1. So we must multiply the figures of the above table by 2.15 to obtain the degree of dissociation at one-tenth of an atmosphere instead of one atmosphere. This holds for the temperatures 1227 and 1727°; for 2227° the factor is actually a little smaller.

The figures given in the table have had great practical use. Water vapor and carbon dioxide are formed when all the commercially important fuels are burned. If, for example, it is desired to determine the temperature which can be obtained by the burning of a certain amount of a fuel in a certain amount of air or oxygen, it must first be assumed that the combustion goes to completion and then one must take into account the equilibrium relations of the combustion gases at the temperature prevailing at each moment of the combustion. Such calculations are made use of in practice for determinations of the power-development in gas engines, and of the gas pressure in guns, etc.

Consideration must be taken of the equilibrium conditions between the reaction products in many other important processes. Nitric acid is obtained in the process of Birkland and

Eyde by heating air in the electric arc. Compounds of nitrogen and oxygen are formed, and these absorb heat in their formation. According to van't Hoff's rule it follows that to obtain the best yield one should use the highest temperature possible. But here there arises the difficulty that during the after cooling of the gases the process reverses and oxygen and nitrogen again separate from one another. The cooling must be brought about as quickly as possible to protect the valuable products from decomposition.

In Haber's process ammonia is prepared from hydrogen and nitrogen. Heat is set free in the formation of the ammonia. On theoretical considerations one ought to obtain more ammonia the lower the temperature. But in this case another difficulty intervenes. At low temperatures the process goes so slowly that the yields are very small. Therefore one must compromise, and use a sufficiently high temperature, 500–600°. In this case higher pressures are advantageous for the yield, since from three molecules of hydrogen and one molecule of nitrogen only two molecules of ammonia are formed, and therefore the volume is decreased to half (from 4 to 2). Very high pressures are used in the process, but of course the strength of the apparatus must be taken into account and this sets a limit on the pressure that can be employed. In practice, pressures of from 150 to 200 atmospheres are used. In experimental work a French investigator, Claude, has used pressures up to 1000 atmospheres, but it is doubtful if this could be applied to large scale operations.

A famous research in these equilibrium fields was performed in 1862–3 by the noted French chemists, Berthelot and Péan de St. Gilles. If acetic acid and alcohol are mixed either as vapor or in solution, (benzol or acetone can be used as the solvent), they change in part into ethyl acetate and water. Ethyl acetate is an ester. The esters are salts which contain an alcohol radical in place of a base. The reaction takes place slowly at low temperatures, but occurs more rapidly at high temperatures. The heat evolved is very small, so the temper-

ature has practically no influence on the point of equilibrium, but only on the reaction speed. If one takes one mol or 60 grams of acetic acid, CH_3 COOH, and one mol or 46 grams of alcohol, C_2H_5 OH, the equilibrium is reached when two-thirds of these materials are transformed into ethyl acetate and water. The two French investigators varied the amount of acetic acid acting on 46 grams of alcohol all the way from 3 grams to 480 grams and each time they determined the amount of ethyl acetate which resulted. Later, in 1877, van't Hoff succeeded in calculating figures which agreed with the values found. He assumed that the equilibrium constant according to the formula of Guldberg and Waage (p. 195) was four, corresponding to a change of two-thirds when equivalent amounts of the raw material were mixed. He found complete agreement. This was in his day the best proof of the equilibrium law, or law of Mass Action.

Equilibrium conditions also play a great role in the chemistry of salts. In fact these were the first to be investigated. As early as 1800 Marggraf found that barium sulfate when suspended in a water solution of an alkali carbonate partly changed to barium carbonate. It was also known that reaction could take place in the opposite direction. In 1853 Malaguti made studies of the phenomena which Marggraf had noted about similiar equilibrium conditions between the difficultly soluble phosphates and chromates with the alkali carbonates. He placed most emphasis on the fact that the two reactions take place side by side in opposite directions, so that in each moment as much of the materials entering into the reaction are reformed as there are of the new compounds formed. Guldberg and Waage's studies of Marggraf's classic investigations became part of the foundation of their law.

However these equilibrium conditions are very complicated. On the one hand the undissolved part of the barium carbonate and of the barium sulfate are in equilibrium with that portion of the chemicals which is in solution; on the other hand the dissolved portions of these substances are electrolytically dis-

sociated, so there is an equilibrium between the ions and the un-dissociated portions in solution. This holds true for each salt existing in the solution, the alkali carbonate and sulfate, as well as the barium salts. In spite of all these complications a simple law can be arrived at, based on theory and experiment by Guldberg and Waage; the amount of alkali carbonate in the solution is in a determined ratio to the amount of dissolved alkali sulfate, no matter how large that may be. A constant temperature must naturally be postulated.

If one adds an acid to a solution of a salt of another acid, for example if hydrochloric acid is added to a solution of potassium nitrate, which is the potassium salt of nitric acid, the added acid replaces a part of the acid of the original salt until an equilibrium is reached. In the case given, which is a very simple one since hydrochloric and nitric acids are both strong acids, equal amounts of hydrochloric and nitric acids are formed if one mixes chemically equivalent amounts of potassium nitrate and hydrochloric acid (see p.35). Julius Thomsen and Ostwald have studied this state of affairs. The former determined the degree of change from the heat developed in the mixing, the latter determined it from the change in volume which occurs. These measurements agreed within experimental error with results calculated from the dissociation theory on knowledge of the electrical conductivity of the acid and salt in question.

As far as our modern observations have gone it is apparent that this condition of equilibrium plays a very important role in physiological chemistry. Thus in collaboration with Thorvald Madsen I have determined that, in the neutralization of a poison by its anti-toxin — for example of the diphtheria toxin by diphtheria anti-toxin, the reaction takes place in quite analogous manner to the neutralization of a weak base by a weak acid, such as that of ammonia by boric acid. Here, as in ester formation, the solvent-water competes with the weak acid or base so that only a part of this is neutralized, while the rest remains free. Since ammonia is a blood poison which can

haemolyse the blood, i.e., can cause the pouring out of the red coloring matter from the red blood cells, boric acid can be used as its antidote. In this way we have made measurements of the neutralization of ammonia with boric acid and determined the degree to which the red blood cells were haemolysed — i.e., how much of their haemoglobin was lost under the influence of the mixtures of ammonia and boric acid. From this we calculated the equilibrium constant according to the Guldberg and Waage law and found that it completely agreed with the constant later calculated by von Lundén from physical-chemical measurements of the decomposition of salts of weak acids and weak bases in water. Conditions of hydrolysis and other equilibrium conditions of electrolytes were discussed by the writer in papers of the years 1884–1888 and 1890.

A very important group of products of plant life are the glucosides, which can be looked upon as sugars (commonly dextrose) which have combined with an alcohol, with the splitting off of water. They are therefore esters, in which the sugar plays the role of an acid. They decompose like ethyl acetate and other esters, with the taking up of water to form sugar (here the acid) and alcohol. They can also be split up more rapidly by certain ferments. Bourquelot and his co-workers have made many studies of these bodies in recent years. He had determined that when they are decomposed with the aid of a ferment a definite equilibrium point is arrived at no matter what mixture one may start with, just as in the case of acetic ester. For example with Bridel he made two different glucosides from dextrose and ethyl alcohol. These were given the names of A form and B form. The first could be decomposed by an enzyme which may be found in air-dried bottom yeast, the second by an emulsin from common almonds. The equilibrium point was reached after a month's standing at room temperature. The A glucoside was 76.6% decomposed; the B glucoside 67.4%. If one went in the other direction and mixed alcohol with dextrose and with the specific ferment the same equilibrium points were arrived at. The course

of the process could be followed by the use of the saccharimeter.

Equilibrium conditions also hold for the partition of two substances between two solvents that do not to any extent mix with each other, for example between benzol and water. Knowledge of these conditions is useful for the study of the partition of haemolysin between the red blood corpuscles and the surrounding fluid, (for ordinary experiments the latter being 0.9% sodium chloride solution), or the partition of the so-called agglutinins found in the body fluids of living animals after bacteria have been introduced, between the bacteria and the salt solution surrounding them.

In the foregoing discussion we have noticed that the course of many chemical processes is aided by many bodies which themselves do not enter into the reaction. This phenomenon appeared most mysterious until it was found to be a not very uncommon occurrence. The English chemist Williamson in 1851 studied such a reaction, which had been written of by Valerius Cordus in 1540 and which is still used for the preparation of ordinary ether from alcohol and concentrated sulfuric. Because of this method of preparation ether used to be called "sulfuric ether." In this reaction two molecules of alcohol give up one molecule of water between them and the rest, or radicals, which result combine together to form a molecule of ether. No sulfuric acid is used up. Berzelius called bodies which act in this way to speed up chemical reactions, "catalysators"; nowadays we say *catalysts*. Williamson concluded from his studies that the ether formation took place in two stages. In the first stage the alcohol combines with sulfuric acid to form water and ethyl sulfuric acid, just as ethyl acetate forms from ethyl alcohol and acetic acid by the loss of water. In the second stage two molecules of ethyl sulfuric acid, 2 $HC_2H_5SO_4$, and one molecule of water give one molecule of ether, $C_2H_5OC_2H_5$, and two molecules of sulfuric acid, 2 H_2SO_4. Thus all the sulfuric acid used in the first stage is regenerated in the second stage. The conclusion was reached

that the action of catalysts could be understood if they were assumed as in the example given, to form intermediate products which later were split down again, into the end-product and the free catalyst, so that the catalyst was completely regenerated. Great advances in the study of the phenomenon of catalysis were made by Ostwald, Bredig and Sabatier. In the case of the catalysts formed by the micro-organisms and by plants and in animal tissue, called ferments or enzymes, a similar addition or formation of intermediate products, followed by decomposition to form end-products, has been noted.

Generally catalytic processes take place sufficiently slowly so that one can determine their time of progress. This means that the speed of reaction can be studied by their aid. In 1777 the German, Wenzel, noted a reaction which took place with measureable speed, namely the dissolving of metals in acids, a reaction which has interested the chemist from the first days that acids were known. This reaction proceeds slowly because in each moment only a very small portion of the metal can be attacked by the acid. Reactions with explosive violence and speed can only take place in solid bodies if they have first been very thoroughly mixed with the bodies acting upon them. Examples are gun-powder, or coal-dust or flour-dust suspended in air, which can explode if ignited.

The study of the progress of a reaction with time has shown that in each unit of time the amount of the substance changed per unit volume is proportional to the concentration of all the reacting molecules and also is proportional to the concentration of the catalyst. Thus for example the speed of reaction of formation of ethyl acetate from alcohol and acetic acid is proportional at the beginning of the reaction to the concentration of acetic acid times the concentration of the alcohol. In the change of cane sugar into glucose and fructose (invert sugar) with the H ion (i.e., an acid) acting as catalyst the amount changed is proportional to the concentration of H ion times the concentration of cane sugar. To find out whether or not an equilibrium is reached, as in the formation of ethyl

acetate, one must also take into account the speed of the reverse reaction going on at the same time. In the case of cane sugar the equilibrium point and the total inversion lie close together, so close that evidence of the reverse reaction back to cane sugar cannot be demonstrated.

These things had been known before the days of Guldberg and Waage but were first formulated by them in their work of 1867, although not in a wholly satisfactory way. Later this was bettered. These laws hold exactly only for very dilute solutions. In higher concentrations deviations occur. This is particularly the case if the catalyst is an organic enzyme such as the inverting enzyme in the inversion of cane sugar, an enzyme called invertase, found in yeast. The temperature has a great influence on the speed of reaction just as it does on the equilibrium point. In the simplest sort of equilibrium such as that between water and water vapor, the density of the vapor at 0° increases as 1:2 for an increase of temperature to about 10 degrees C. In about the same proportion or up to 1:3 the speed of reaction increases at each increase of 10° in the range of ordinary temperatures. But higher values for the influence of temperature are sometimes to be found, particularly in the case of the spontaneous decompositions of organic substances. Thus Madsen and his pupil found a speeding up of the reaction of decomposition of a haemolysin at about 50° C. in the ratio of 1 to 1000 for each ten degrees increase of temperature. Of course that is an extreme case. This influence of temperature explains the well known fact that increase of temperature favors chemical reaction in general. In many industrial processes due consideration of this fact must be taken. Here the rule holds good that "time is money." A process which at 0° would be quite un-economical may give excellent results at 40–50°. The value of catalysts also lies in the fact that they speed up reactions, and they have therefore played a great role in industry.

We have spoken above of the Haber process. Its economic success was absolutely dependent on the use of catalysts.

Haber first used osmium or uranium preparations, but these were very expensive so he sought for other catalysts and chanced to find that certain iron preparations — iron oxide containing a little arsenic oxide, would replace them and left nothing to be desired as to cheapness of the process. Another example from big industry is the manufacture of sulfuric acid. In the eighth century the Arabic chemist, Geber, knew of this acid. For a long time, until the introduction of the lead chamber process by Roebuck in 1746, sulfuric acid was made by igniting iron vitriol or alum, both of which are sulfuric acid salts. The fuming sulfuric acid so obtained was called "oil of vitriol." In the lead chamber process nitric oxide was the catalyst which brought about the more rapid combination of sulfurous acid with oxygen. The sulfurous acid was made by burning sulfur or by roasting pyrite. This gas which is known by its choking odor to every one who has ever burned one of the old sulfur matches, was mixed in the lead chamber with air, water and a little nitric acid. The nitric acid oxidized the sulfurous acid to sulfuric anhydride (SO_3) which, when dissolved in water, gives sulfuric acid, H_2SO_4. By giving oxygen to the sulfurous acid the nitric acid, HNO_3, changes to nitric oxide, NO, and water. The nitric oxide has the valuable property that it can take oxygen from the air and then the oxide so formed, NO_2 or N_2O_4, can again give up oxygen to a new portion of the sulfurous acid, again forming nitric oxide, NO, and so on. The chamber acid has a content of 60 to 70% sulfuric acid. This was formerly concentrated in platinum vessels, but since the latter metal has become very expensive this has been replaced by vessels of lava, or of fused silica. But a new method has been devised for the direct preparation of the very useful concentrated sulfuric acid, and this was very largely used during the war. It is called the contact process and depends on the property of finely divided platinum which can bring about formation of sulfuric anhydride (SO_3) in a mixture of sulfurous acid and oxygen passing over it. For this process the gases from a pyrite roasting oven are led, mixed with air and at a

temperature of 400–500°, over platinized asbestos or platinized iron-oxide. The resulting anhydride is led into chamber acid which absorbs it and the product is called fuming sulfuric acid, the same product which was obtained by the very oldest process of manufacture. The fuming acid, needed in certain processes, can be changed into ordinary concentrated sulfuric acid by dilution with the proper amount of water. In the same way finely divided platinum can also be used as a catalyst in various other processes, for example in the preparation of acetic acid from alcohol. But unfortunately platinum is not cheap. Furthermore it is easily "poisoned," that is to say it loses its valuable catalytic activity when it comes into contact with various impurities in the gases used. It is particularly liable to damage by arsenic, which is often present in the pyrite and passes into the gases when the mineral is roasted to supply sulfurous acid for the contact process.

In the Haber process the catalyst can be injured by poisons. Sulfur, selenium, tellurium, phosphorus, arsenic, boron, and their compounds are active poisons of this catalyst. Carbon monoxide generally has a detrimental effect on the iron catalyst by precipitating carbon in it. On the other hand the activity of the iron can be increased by the presence of various oxides, especially by magnesia. The best temperature is 500–600° and the best pressure in practice is 150–200 atmospheres. The catalyst works best if deposited on asbestos. At the ordinary circulation speed of the gases about 10% of the hydrogen and nitrogen mixture is changed into ammonia.

By a method devised by Ostwald and developed by Van Brauer the ammonia obtained in the Haber process can be oxidized to nitric acid. A mixture of ammonia and air at 500-600° is led over platinum sponge. A portion of the ammonia is lost by decomposition into hydrogen and nitrogen. Many attempts have been made to avoid this difficulty, without success. By rapid passage of the gases over the catalyst the losses can be made as low as possible.

One of the most important catalytic processes should be

mentioned, the process discovered by Sabatier in which hydrogen is led into liquid fats such as olive oil, linseed oil, cotton seed oil, fish oils, etc., whereby solid fats result. The catalyst in the "hardening" of fats is finely divided nickel, or a nickel compound. As one result of the reaction these oils lose for the most part the evil odor and taste which many of them, especially the fish oils and cod-liver oil, may possess, but, unfortunately they may gain these again on standing. Nickel and its compounds act best as catalysts around 200° C. Platinum, also used for these hydrogenation processes, works best below 100° C. Naturally nickel is much used in practice because of the lower cost. By increasing the pressure the temperature of the reaction can be decreased. The nickel can also be spoiled by poisoning. Hydrogen can be removed from, as well as added to, organic substances by this process of Sabatier. Large factories have been erected for the preparation of solid nutrients such as lard substitutes, etc., and for making stearin and soap, with the aid of this process.

A characteristic catalyst, used in the preparation of methyl-violet from dimethylaniline, and in various other organic syntheses, is copper metal. One wholly unexpected case of catalytic action was discovered by accident. When naphthaline was being heated with sulfuric acid to make phthalic acid, a mercury thermometer which dipped into the vessel was broken. It was soon evident that the reaction was greatly speeded up by the presence of the mercury, and since then this catalyst has been found very useful in other similar reactions.

In sum the most important catalysts are: hydrogen ion and hydroxyl ion, yeast ferments, finely divided platinum, nickel and iron, aluminum chloride, Grignard's magnesium reagent for organic syntheses and the proteolytic ferments which act in the digestive processes of animals.

Water vapor has a noteworthy action in chemical reactions. In many cases it need only be present in very small quantities to catalyse a reaction. It is known that a mixture of oxygen and hydrogen will explode on heating it to about 600°. But

the presence of a trace of water is necessary. If this is carefully removed by long treatment of the gases with phosphorus pentoxide, the mixture can be heated to 1000° without explosion. The English workers, Dixon and Baker, have studied a great many such catalyses by water vapor. A case of this sort in industry is the preparation of calcium chloride from slaked lime and chlorine — this is much aided by the presence of a trace of water.

Industrial chemistry has only begun to make really scientific use of catalysts, yet catalytic methods have already found wide spread use in practice. We can safely say that catalysts in the future will show themselves capable of still greater service than they have yet given.

Chapter XII

DYES, PERFUMES AND DRUGS

Up to the end of the 18th century the development of chemical industry proceeded rather slowly. From that time on it took a great stride and it was England especially which took a leading position in this field, a field which has been of the greatest influence in modifying and enriching our culture. At first the principle products of chemical industry were the metals, soap, and a few dyes, especially indigo, and the "royal color" purple. In the very earliest days people clothed themselves in animal furs, later for the most part in clothing derived from animal material, mainly leather and wool together with some silk and a little linen. It was known how to bleach cloth in sunlight and moisture, and how to tan leather, for which purpose some alum was used. To dye with madder root, iron vitriol and alum were employed. Soap was prepared from wood-ashes or the ashes of sea weeds or, since the very earliest times, from the deposits of the salt-seas.

The amount of these useful things, handled in commerce as compared to our present trade, was almost none at all, and from this we can gain a picture of how our ancestors must have lived. Chemicals were transported in commerce to a far less extent than now. At the end of the Middle Ages, when gunpowder began to be used in waging war, a little change came about in this state of affairs. Gunpowder was known of course far earlier than this in the form of Greek-fire, which had been used in the defense of Constantinople from seige by the Saracen navy in 673 A.D. For this Greek-fire charcoal, sulfur and saltpeter were used according to a formula which was held as a state secret. Charcoal was made from wood, sulfur was found in large quantities in Sicily, only the saltpeter was scarce and

hard to obtain. In southern lands such as Egypt and India potash saltpeter often weathered out on earth of high humus content. It was collected and recrystallized and was, according to the reports of Geber (dating from about 702–765 A.D.), at his time an object of commerce. As a result of the growing needs for it, attempts were made to improve upon Nature's method of preparation. "Saltpeter plantings" were made by mixing nitrogenous refuse from abbatoirs with dirt, ashes and chalk and letting decomposition take place, in which process bacteria formed nitrates. In stables and stalls saltpeter gradually formed from manure, which was leached with water and the liquor evaporated till the saltpeter crystallized.

It is interesting to see how this simple and primitive chemical process of the barn-yard has affected the politics of Europe. In Germany and particularly in the Black Forest district the men who were skilled in this process once had considerable political influence. Thus in 1727 a political society called the "Saltpeterers" under a leader named Albiez sought freedom from the jurisdiction of the Abbé of St. Blasien. These efforts and later uprisings were quelled by the Austrian police. Later the movement took on more of a religious character. As late as 1830 we hear of the "Saltpeterer's" influence in the problem of the Bavarian government. In Sweden, the first king of the united land, Gustav Vasa, ordered all farms to leach out saltpeter for the use of the state in the manufacture of gunpowder. A sort of tax of saltpeter was laid. It was permitted to buy oneself from the levy with money, but the average farmer probably preferred to contribute his 4.25 kilos of raw saltpeter per capita. This tax was only lifted in 1830.

About 1825 a soda saltpeter was introduced from Chile and this soon replaced the ordinary "saltpeter earth." From the saltpeter by heating with alum or iron vitriol nitric acid should be obtained. This latter was called "parting water" because, by its use, one could separate gold from silver. On this account it was of great use in minting.

In the 18th century material culture gained rapid advance

especially in France and England, and there came about a great need for soda (sodium carbonate) which was of use in glass manufacture and in soap manufacture. The French Academy of Science offered a considerable prize for a method of preparing soda from common salt. The surgeon, Leblanc, (1742–1806) solved this problem and the first soda factory using his process was erected in 1793. During the French Revolution this was confiscated by the committee of public safety and as a result the soda industry of France died out. The art passed over to England, where the first soda plant of Muspratt was started in 1824. Leblanc died in misery at an almshouse in 1806.

At about this time a factor appeared which was to be of greater importance for the future of chemical industry than any other — this was the increasing use of cotton. This, the most important of all textiles, had been grown in India from primitive times and was used there for the preparation of cloth. After the invasion of Alexander the Great its cultivation spread to Greece, and little by little to all the Mediterranean lands. In Western Europe cotton mills were first started in Holland and later in England. At the end of the eighteenth century the cotton industry had reached a high state of development and was soon to receive still greater impetus from the produce of the American plantations, and by the invention of the first successful cotton gin by Ely Whitney of Westboro, Mass. Whitney received his patent in 1779. No other industry has ever been the cause of as great an economic, social and political revolution as has the spinning of cotton.

This industry required amounts of sulfuric acid, soda and calcium chloride such as had not been conceived of before. The chemicals were used in the bleaching, dyeing and printing of cotton goods. The demand of this industry for sulfuric acid resulted in a new "lead chamber process" for its manufacture. Leblanc's process filled the need for soda. This process also led to the preparation of hydrochloric acid, which at first was a very burdensome and undesirable by-product, but soon came

to be employed in bleaching-powder manufacture. At just this period also illumination by gas began to come into use and there was obtained as a by-product the evil-smelling substance known as coal tar. This was thrown away at first. Its value was disclosed by the German chemist, Runge, in Berlin (1834). He noted that among the constituents of the black mass there were to be found aniline, phenol and pyrrol. A. W. Hoffman in 1825 identified the constituent today the most useful, benzol, a substance which Faraday had already isolated from the illuminating gas itself. Perkin, in England, in 1856, was the first to make a dyestuff, *mauve*, from a coal-tar constituent.

As a result of England's leading position in the cotton industry, "big-business" in chemicals now rapidly developed. Sulfuric acid, soda and bleaching powder became articles of a world-wide commerce and the national welfare of the island nation was based upon its leading position in this field. This lasted till the end of the last century when the Solvay ammonia-soda process and the electric methods of preparation of soda and chlorine brought about the complete failure of the old industry. Its collapse and the consequent neglect of the working up of coal-tar in England, gave to Germany its world-dominating position in the coal-tar industry.

The Leblanc soda process depends on the driving of hydrochloric acid from sodium chloride by the action of sulfuric acid, sodium sulfate being formed. To make neutral sodium sulfate the mixture must be heated in a furnace, otherwise only acid-sodium sulfate is formed. This latter is a salt which stands half way between sulfuric acid and sodium sulfate. Now to get soda from the sodium sulfate, the sulfate in the latter must be replaced by carbonate. This is effected by heating the cheapest and commonest salt of carbonic acid, limestone, with the sodium sulfate in the presence of about half their amount of carbon. In the presence of the carbon the calcium sulfate, gypsum, which is formed, is reduced to calcium sulfide which remains mixed with the soda while carbon dioxide gas passes off.

On removal of the melt from the oven and after cooling, the

soda is leached out by water, while the calcium sulfide which is only slightly soluble in the presence of lime, remains behind in solid state. The hydrochloric acid, which forms during the preparation of the sodium sulfate from the common salt early in the process, is taken up in the water and later mixed with manganese dioxide for the preparation of chlorine. This gas is taken up by slaked lime and forms chloride of lime. It is this employment of the formerly useless hydrochloric acid which today enables the Leblanc process to compete with the Solvay process. Many of the old soda factories, however, have given up making soda, and prepare only sodium sulfate, Glauber's salt, for use in the glass industry, and then make bleaching powder from the hydrochloric acid released in the preparation of the sulfate. The need for bleaching agents has become much greater in recent years because of the great growth of the cellulose and paper industries.

The Solvay process is as follows: An "equivalent" amount of ammonia gas is led into a saturated solution of common salt. This latter solution is pumped from the earth in regions where underground salt deposits occur — water being led down into these layers to form the solution. Then the ammoniacal solution is saturated with carbon dioxide (from gases from the lime kiln and from combustion gases) so that acid sodium carbonate, sodium bicarbonate, precipitates, and sal ammoniac, ammonium chloride, remains soluble in the liquor. From the sal ammoniac the ammonia content is recovered by treatment with milk of lime, — calcium hydroxide. The sodium bicarbonate is heated, whereupon water and carbon dioxide pass out of it and soda is left. The carbon dioxide is used over to be led again into the ammoniacal salt solution. The actual net results of the reaction therefore are that slaked lime with carbon dioxide and sodium chloride form soda and calcium chloride. This latter is almost useless — there is no large industrial demand for it. A little of it is dried and used to remove water from solutions, i.e., as a drying agent, but the main mass must be dumped into the river.

The part which is played by the ammonia in this process is the formation of the intermediate ammonium carbonate, in order to separate by precipitation the difficultly-soluble sodium bicarbonate from the rest of the reaction mixture. Soda, however, is very easily soluble, about 3.5 times more soluble than sodium bicarbonate at 30 degrees C., so that it cannot be directly precipitated in so easy a manner. This Solvay process which has been developed since 1865 makes use of extremely cheap raw materials. Especially is this true in such lands as possess deposits of rock salt. Thus it found a natural home in Germany, but because of its economy this process is also used in many other lands. In countries which have cheap water power the preparation of soda by an electrolytic process can successfully compete with the Solvay process, and this it can do all the more successfully because it furnishes chlorine directly without the intermediate use of manganese dioxide.

From all the above we may readily see that the dyestuffs industries because of their importance for supplying the needs of the dominating industry of textiles, have been a stimulus for the development of big-business in general. Germany obtained its powerful position in these fields before the world-war as a direct result of the introduction and use of the ammonia-soda process and the contact-process for sulfuric acid and above all by her furtherance of the coal-tar industries, in consequence of which English chemical industries were forced in the background. In 1910 there were 2,000,000 tons of soda made in England, 400,000 tons in Germany, 250,000 tons in the United States and 20,000,000 tons in France. In the same year the 5,000,000 tons of sulfuric acid which constituted the world output were divided between the four countries as follows: England 1,000,000, Germany 1,250,000, U. S. 1,200,000, France 500,000 tons. The saltpeter production of the world was 2,360,000 tons and out of this England used 93,000, Germany 786,000, the U. S. 523,000 and France 337,000 tons. Germany and the U. S. had in 1910 surpassed England in the heavy chemical field in every way. Today, post-bellum, the U. S.

hopes to take the dominating position in these fields just as she now holds it in the field of the metals.

Equally a lesson is the story of how Germany acquired the monopoly of the manufacture of alizarin and indigo dyestuffs, which from the Middle Ages were the principal colors used in oriental rugs and other cloths. For the artificial manufacture of these dyes the raw material is coal tar. The most important aromatic compounds contained in coal tar are benzol (and toluol) 3%, phenol 1%, naphthalene 5% and anthracene 0.5%; all these figures are approximations, for the composition of the tar depends on the sort of coal from which it is distilled. Altogether these valuable constituents make up about ½ of 1% of the total bulk of the primal raw material, fossil coal.

As early as 1868 two German chemists, Gräbe and Liebermann, succeeded in making the valuable mordant dye material — *alizarin*, out of anthracene (which has the formula $C_{14}H_{10}$). By oxidation of the anthracene they got a body, anthraquinone, of formula $C_{14}H_8O_2$. Two oxygen atoms have entered into combination with the anthracene and two hydrogen atoms have been removed. If the anthraquinone so formed is heated with sulfuric acid, and thus oxidized further, another pair of oxygen atoms enters the molecule and one obtains *alizarin*, $C_{14}H_6O_4$, which is identical with the body that is the principal color-substance of the madder root. Between the years 1870–77, 750 tons of alizarin were extracted from madder root. In the year 1873, 100 tons were made artificially, by 1884 this had increased to 1350 tons per annum, and in 1900 to 2000 tons. Great tracts of land in the Mediterranean countries, particularly areas near Avignon in France, which for many years previously had made great profit out of the growing of madder root, were forced by the competition of the synthetic product to give up this crop and had to be converted to the growing of other crops, naturally with great economic loss. However, seen from a more general point of view than that of the Avignon madder growers this must be looked upon as a benefit, for a fruitful district was thus returned to the ranks of bread-producing regions.

Yet greater economic interests were ruined by the successful artificial production of indigo. This most important of all the dyestuffs has been in use from the grey dawn of antiquity by the Egyptians, the Phoenicians and the Greeks. Indigo can be prepared from many different plants of which the most important is *Indigofera tinctoria*, a plant which originated in the East Indies but today is spread by cultivation into many parts of the tropics, in Asia, Africa and South America. Another indigo-plant, *Isates tinctoria*, the *woad*, is much hardier and is to be found growing in Europe as far north as Sweden. It was formerly, especially around the year 1300, an object of intensive cultivation in France and Germany, but as indigo began to be imported from the East Indies its European cultivation died out. Probably ancient man in Europe used the woad for a blue dye from very early times. The Pictish people of North Britain, when found by the Romans, were in the habit of painting their bodies for battle with woad. Indigo production in India in the past century was one of the most important sources of revenue of that country (and, in consequence, of England). In 1897 the total value of natural indigo production was 20,000,000 dollars, and the amount was 6 million kilos of pure indigo, of which 90% came from British India.

In 1880 the famous German chemist, A. Baeyer, succeeded in preparing synthetic indigo from naphthalene. However, it was not till 1897 that the process was sufficiently perfected to compete with natural indigo. The research work on which this successful result was based had cost about 5,000,000 dollars. It was principally carried on by the scientific staff of the Badische Anilin and Soda Factory. Naphthalene was first changed to phthalic acid by warming it with sulfuric acid. In the investigation of this process an accident, the breaking of a mercury thermometer into the pot, led to the discovery of a catalyst, mercury sulfate, which has since made possible the economic success of the process, (see p.211). Six stages of manufacture after that of phthalic acid are necessary before the dyestuff, indigo, is obtained. In the process great quantities

of sulfuric acid are lost, for after giving up its oxygen the remainder passes off as sulfur dioxide gas. To regain sulfuric acid from this gas, Winkler discovered the contact process. Also the manufacture of indigo used up large quantities of chlorine gas, and for the preparation of this latter the method of electrolytic manufacture was shortly introduced. All these interlocking processes serve to illustrate what a marvellous amount of intelligent and persevering work must be done in solving problems of technical chemistry such as the above.

But the results were most satisfying to the perservering workers. The importation of indigo into Germany sank from a value of fifty million dollars in 1896 to a value of eighty thousand dollars in 1911, while the export from that country for the same period mounted from thirteen to one hundred million dollars in spite of a drop in price to less than one-fifth. At the same time the value of the export of indigo from British India sank from seventeen to one million dollars. At one time the surface given over to the growing of indigo plant in India was not less than 1,480,000 acres.

At this point it may be noted that a German investigator, Paul Friedländer, discovered that the Tyrian purple of the ancient world was a derivative of indigo — dibrom indigo. This dye had already been made in the laboratory but had attracted no attention, being of inferior beauty to many other artificial dyes. Friedländer extracted the dyestuff from 12,000 snails of the species, *Murex brandaris*, which according to the account of Pliny is identical with the snail that furnished the ancient purple. In this manner he obtained just a gram and a half of the material, so we can see how valuable the ancient dye must have been. One can calculate that the dyestuff today, if obtained in this way would be worth about $10,000 per kilo and the dyeing of a royal robe would cost many thousands of dollars. It was the special privilege of kings to use this dye, and its praises are sung in flowery words by the classical writers. Today even the poorest man could buy himself clothes dyed with this purple, but he would not wish to do

so for the purple of the ancients is far surpassed in beauty and sheen by many well-known synthetic dyes of today. It is quite possible that the desirability of the purple in ancient times depended largely upon its enormous price and scarcity. Many circumstances show that most of the men of that day, although they are often praised for their classical tastes, still set their chief aim on those things of most stupendous price. The profiteer of today has his ancestral avatar.

By replacing the nitrogen atoms of indigo with sulfur, Friedländer made a dyestuff of a useful red color, called indigo red. Another related derivative is called thio-indigo-scarlet. In the search to make from anthracene dyes of analogous composition to indigo, Bohn discovered in 1901 a new class of dyes, the indanthrenes. Among these there is a blue dye which resembles indigo but which differs from it in beauty and especially in not fading so easily in the light. Indeed it can be said to be completely light-fast. Similarly R. Schmidt discovered by chance that a series of dyestuffs of complete stability to light could be made from amido-anthraquinone. These are called the algol-dyes. Like the indanthrenes they can be made to give all possible colors and shades. In the same way the manufacturers of the so-called azo-dyes, which had been discovered by Peter Green in 1869, found out how to make a new group called "Benzolicht" dyes which really are not absolutely nonfading dyes but still are very useful and have quite largely taken the place of the formerly well-liked benzidine dyes.

The first coal-tar dyes such as the mauve discovered by Perkin in 1856, the fuschin, which was much used at first, discovered by the French investigator, Verguin, and the immediate followers of these dyes, were all truly far superior in glance and sheen to the old natural dyes of similar shade, but they had the common fault that they all faded easily. In some of the new groups of dyes this condition of affairs is practically completely done away with, so that the dyes successfully compete with natural colors both in stability and in color-glance. By

the substitution of various groups in place of those normally entering the composition of a dye, various shades and colors as desired may be made, and it can even be calculated beforehand whether the change of chemical composition will lead the color, for example from red through orange or yellow to green, blue or violet, or in the opposite direction.

Nearly two thousand different coal-tar dyes are known and among them there are some which cannot be spoken against in any way, as to non-fading qualities, fastness to washing, and in color-tone. One may look upon the preparation of the most valuable and useful of dyes in all the colors and shades of the spectrum, from the dirty and ill-smelling coal-tar, as one of the higher triumphs of modern science, for it has given us dyes which are more lovely than the lilies of the field.

Here it may be noted that the substances which have a high degree of fluoresence also belong in this group of the coal-tar colors. Among these a substance called fluorescein has taken its name from this property alone. It is a dye made from resorcin, a comparatively simple chemical, which is combined with phenol and phthalic acid. The fluorescein, like phenol itself, is an acid. Its salts with alkalies have an extremely intense green-yellow color. Fluorescein is the raw material for a group of strongly colored and fluorescent dyes, among which may be named the brom derivative, tetra-brom fluorescein. This is a stronger acid than the mother substance and gives alkali salts of extremely great color-intensity. The potassium salt is called eosin, and its water solution is used to dye wool and silk to a useful, rose-red color.

Because of its intense color fluorescein is used to explore the underground connections between water courses. Thus for example the Donau river between Immendingen and Möhringen in the Swabian Jura loses part of its water as it passes through a porous chalk layer. People believed that this water reappeared 11 kilometers further south in the village of Aach, for an underground stream there rose to the surface and flowed out into Lake Constance. By placing a fluorescein solution in the

Donau river water at the point where it disappeared in the chalk cliffs and then by observing the color of the water flowing out at Aach it was possible to prove the connection between the two water courses.

The late Emil Fisher, German chemist of considerable fame, in fact a scientist who contributed more than any other of his day to the development of organic chemistry, at one time worked with the various fluorescein dyes. In this period he once went to a public bath and took a dip in the big swimming pool. As he left the water he overheard other bathers complaining of the dirtiness of the water of the pool. It had acquired a powerfully fluorescent yellow-green color. Fisher, who believed that the color must have come from some flecks of fluorescein which had probably fallen in his hair while in the laboratory, forebore from giving any scientific explanation to the group — and he suddenly decided to return to his laboratory as quickly as possible!

Fluorescein is a near relative to phenolphthalein, which is well known to all workers in chemistry because of its use as an indicator for the presence or absence of acid or alkali in water solutions. The property of an acid which we call sourness depends on the presence of hydrogen ions in the solution. Phenolphthalein is colorless but its alkali salts possess in solution a weak carmine color. If a trace of a strong acid is added to the water, let us say, for example, hydrochloric acid, to such an amount that a one one-hundredth normal solution results, then the hydrogen ion concentration is 0.0001 or 10^{-4}, which latter is the way mathematicians abbreviate it. Now if to this solution a drop of alcoholic phenolphthalein solution is added, the phenolphthalein which is only soluble with difficulty in water is thrown out of solution, but is not seen because it is colorless. If now alkali, for example a solution of sodium hydroxide of given normality is added to the solution drop by drop from a graduated vessel called a burette, one notices a sudden change of the color of the solution to carmine, and this occurs when the amount of alkali added is precisely correct to

neutralize the amount of acid in the solution. This happens when the amount of alkali is the chemical equivalent of the original amount of acid in the solution. By electrometric measurements, a method based by Nernst on the theory of electrolytic dissociation and on a resulting theory of "concentration-elements," it has been found that this carmine color makes its appearance when the hydrogen ion concentration sinks to 8×10^{-10}.

So by means of this indicator one can determine whether the hydrogen ion concentration of a given solution is greater or less than 8×10^{-10}. By the aid of another dyestuff which gives a color change at a different known hydrogen ion concentration it can then be determined whether this concentration lies above or below the boundary line of color-change of the second dyestuff. A scale of the dyestuffs has been made for determining the hydrogen ion concentration of water solutions within certain known intervals. According to this method, which was mainly developed by the Danish chemist, P. L. M. Sörensen, the hydrogen ion concentration of solutions can be found in a much simpler and quicker manner than by electrometric measurements, provided the solutions themselves do not have too strong a color. In this latter case, which is fortunately rather rarely met with, it is necessary to fall back on the electric methods.

Indicators composed of plant coloring-matters—first an extract from the flowers of violets, and later litmus, which is obtained from a lichen—have been used by chemists, from as early a time as the 7th century. The reader may ask what use it is to know the hydrogen ion concentration of solutions. It may be answered that we today recognize that all life is influenced to a high degree by hydrogen ion concentration. Thus the ability of a ferment to act has an optimum at a given hydrogen ion concentration. Bacteria and fermentation-fungi, which play an important part in our daily life, grow best, and therefore have most powerful effects, at hydrogen ion concentrations specific for each kind of these plants. The ferments of the stomach also

have an optimum at a given hydrogen ion concentration, which is determined by the hydrochloric acid content of the digestive juice, and a change in this can derange the digestion and completely ruin the health. Similarly the hydrogen ion concentration of the various body fluids such as those secreted by the glands, or the lymph, or especially the blood, require a certain characteristic concentration in order that their life-chemistry can proceed normally. The presence of certain acid salts — especially the phosphates and the carbonates, as well as the presence of "amphoteric" (i.e. both acidic and basic) albuminous substances in the body fluids act to regulate and stabilize the normal proper hydrogen ion concentration of these fluids. The whole chemistry of life is dependent on hydrogen ion concentration. It rules over health and sickness and over life and death.

It would almost seem that these every-day, weakly-colored dyestuffs which serve as indicators have been of greater use to man, as Nobel has claimed, than all the intense colors which the coal-tar dyes can lend to the fabrics of our clothes and our surroundings. And yet there are comparatively few investigators today who study the importance of hydrogen ion concentration, while the great majority of men, instinctively and without reflection, have the highest regard for the dye-industry, which we are well able to control through our knowledge of the coal-tar colors. The manufacture of these dyes and the various industries connected with their commerce have had extremely great effect upon business and upon economics. They have led to economic and diplomatic machinations and intrigues and have been the cause of national misunderstandings and have served as contributing factors to national armaments. It is the best evidence of how deeply rooted are the esthetic needs of man that he should make such a demand for dyes. Such needs are indeed primal. Instincts for bright colors are to be found strongly developed even among the animals. We find that the Magdalena people who were alive on this earth 25,000 years ago covered their cave-dwellings with fine wall-

paintings and painted their bodies, when they prepared for war or for a wedding dance, with dyes which they found at hand from plant and mineral sources about their dwellings.

Another esthetic need is filled by the perfumes. Most of these have required a knowledge of organic chemistry for their preparation. The most important natural perfumes have been found in flowers, from which they can be distilled by steam and so concentrated. In other plant-parts perfumes also occur. Most such perfumes belong to the terpene and camphor like substances. The German chemist, Wallach, has contributed more than any other individual to the building up of the chemistry of these essential oils and has thus laid a scientific ground-work for their preparation in a synthetic way. Large factories have arisen in Germany and in other lands. Many of the pleasant smelling oils, such as rose oil are obtained by the distillation of water with the flowers. Other oils are prepared artificially, for example lilac essence, which is made from turpentine oil by changing it into terpineol.

Many odorous substances can be made from benzol and its derivatives and for this reason these chemicals are often called aromatic compounds. They also occur in the pleasant smelling oils of the plants, from which they were formerly isolated as perfumes, but today most are manufactured synthetically. Among these, anethol is found in anise oil, menthol in peppermint oil, and thymol in thyme oil. Cumarin, which is the odorous substance in the melilot, in *asperula odorata* and in the tonka bean, is prepared almost wholly synthetically by heating together phenol and malic acid, and similarly vanillin, which is the principal perfume and flavor of vanilla, is made from the glucoside, coniferin, which is to be found in the cambial-sap of coniferous trees. Further there are heliotropin and ionon, the odor-substances of heliotrope and of violet flowers, and also cinnamyl-aldehyde which is to be found in cinnamon and cassia oils. Many of the artificial perfumes are mixtures of many things, thus artificial rose, lily of the valley, and violet-flower oils must have several constituents each, in order that the odor

may approach the natural one. A few of the perfumes have no relation to the similarly-odored natural products whose name they get only because of this similarity. Thus there is orchid essence, whose scientific name is amyl salicylate, and the artificial bitter-almond oil, nitrobenzol, sometimes used for perfuming soap. A few perfumes are prepared from the fatty acids — thus ethyl acetate or the butryate, called banana essence, amyl isovalerate, called apple essence, and amyl acetate called pear oil. These are principally employed for the flavoring of refreshing drinks, and to give taste to candies and artificial wines.

Because of the manufacture of synthetics the price of these goods has sunk greatly. Thus the prices of vanillin, coumarin and heliotropin, which in 1875 were $1600, $24 and $720 per kilo, had sunk in 1911 to $7, $6, and $2.40 per kilo. One can also consider camphor as a perfume. Schering succeeded in making Japan-camphor from terpentine oil. This is of great importance for Japan previously had a monopoly of this valuable substance — which was extracted by distillation from a plant, *Laurus Camphora*, that grows especially well in Formosa. The camphor is used quite largely in industry for the manufacture of celluloid, and it also is used in medicine.

From primitive times the peoples of even the lowest culture have discovered medicinal properties in various plants and have used them either as the whole herb, or for the preparation of decoctions, to mitigate or heal sicknesses. Pharmaceutical chemistry sprang from the study of the medicines of the plant and animal kingdoms, although some preparations were also made from inorganic nature. Today we seek more and more to replace these drugs with pure, synthetic preparations, whose compositions are no matter of doubt. As early as 1831 the French worker, E. Souberain, prepared the important anæsthetic agent, chloroform, $CHCl_3$, by distilling alcohol with chloride of lime. Somewhat later in the same year, Liebig also got this substance as a result of the distillation of acetone with chloride of lime.

In the year 1010 A.D. the Arab doctor, Ali ben Isa, mentions an anæsthetic agent, i.e., a narcotic — used to lessen the pain of eye operations. Probably this agent contained a preparation of the "witches root" — the mandrake, used from the days of grey antiquity and spoken of in the first book of Moses, or it may have contained opium, spoken of by Homer in the Iliad as a substance consecrated to Morpheus, the God of Sleep. In 1150, Nikolaus, leader of a school of medicine in Salerno, included in his antidotarium a discussion of the inhalation of vapors from narcotic plant-materials. This book may be considered as the first European pharmacopœia. Such agents as the above mentioned were made use of when surgical operations were necessary. In 1844 Wells described the first actual anæsthetization with laughing gas (nitrous oxide), which had been discovered by Priestley. Next, in 1846, the Americans, Jackson and Warren, employed ether as an anæsthetic, but this was shortly displaced by the use of chloroform as a sleep-producing agent. Ether is the safer substance for general narcosis, however. Liebig was the first to make chloral hydrate, $CCl_3CH(OH)_2$, by treating alcohol with chlorine. Its sleep-producing ability was discovered by Liebreich in 1869 and it has been used considerably in medicine ever since. A near relative chemically of chloroform is iodoform, which was first prepared by the French chemist, Serullas, in 1822, but it did not come into use as an antiseptic until about 1870.

Glycerin is the source from which is produced today in technical quantities one of the most powerful of all the pain-deadening agents, *alypin*, which may be locally injected before operations in order completely to prevent the sensation of pain in an area of the body. Although these medicines cannot be looked upon as actual remedies they (especially ether and chloroform) have contributed very largely to the mitigation of human pain and suffering.

The first actual medicine to be prepared synthetically was salicylic acid, which can easily be gotten out of salicin, a substance which is to be found in white poplar and willow bark.

Decoctions of such bark have long been used for a remedy in rheumatism. In 1860 Kolbe, by the action of carbonic acid on the sodium salt of phenol — commonly called carbolic acid — made the substance, sodium salicylate, which is also itself used in medicine and which can easily be converted into the free salicylic acid. From the sodium salt, by the action of acetyl chloride there is prepared the sodium salt of acetyl-salicylic acid. This material, one of whose trade names is Aspirin, has the same valuable properties as has salicylic acid, but without some of the undesirable properties possessed by the latter. It was first introduced into commerce by the firm of von Heyden in Dresden. This drug has found considerable use not only in fighting rheumatism and gout, but also especially against influenza, neuralgic pains and for lowering the body temperature in fevers, etc.

Another useful agent for fighting fever and neuralgia is called *antipyrin*. This was discovered by Knorr. *Pyramidon* is a derivative. A third similar agent is *acetanilid*, which was found to have useful fever-reducing properties by two young medical students, Cahn and Hepp. They were making a study of the physiological activity of naphthalene and they found that the preparation they were using lowered the body temperature. But further trials with naphthalene from another source did not give the same result. They then discovered that, the first time, the chemical supply house had given them acetanilid by mistake and that this had produced the desirable, febrifuge effect. The new medicine was given the trade name of antifebrin. It showed certain toxic symptoms, so an alcohol-derivative of it called *phenacetin* was made, which showed less-marked poisonous properties, yet had the same desirable properties as the acetanilid.

In America and England, use has been made of the odorous oil of winter-green as an agent for lowering fever. This oil is obtained by distillation of an evergreen plant of the American forests — *Gaultherea procumbens*. Oil of sweet birch also consists almost wholly of the same chemical. It has been replaced to-

day by the use of a synthetic oil, which consists of the actual active principal of the natural oil, *methyl salicylate*, which can easily be made by combining methanol and salicylic acid. This oil has the property of lowering the body temperature in fever. It can be rubbed into the skin, while the other fever-reducing medicines must be given by mouth. It has the advantage also that a powerful local action can thus be exerted. But its strong odor is a disadvantage, so it has been replaced to some extent by another volatile ester of salicylic acid, which is almost odorless. This has the trade names of Mesotan or Spirosal.

Emil Fisher prepared synthetically the alkaloid which occurs in cocoa, theobromine, and the two which occur in both tea and coffee, caffein and theophylline. Of these three bodies belonging to the purine group, the first two are prepared nowadays in large quantities by extraction of the cocoa bean with ether, and of the coffee bean with benzol. In the latter case the residue becomes the "*caffein-less coffee*" of commerce. The drugs thus obtained are used as diuretics, (substances which increase the flow of urine), and are prescribed in cases of dropsy.

There was anciently employed as a styptic in gynecology a drug extracted from the American plant, the Golden-Seal, Hydrastis canadensis. The active agent here is known as *hydrastin* and constitutes from 2.5 to 4% of the dried drug. The hydrastin is today prepared from the sweet-odored, synthetic chemical, *heliotropin*, used in perfumes. Aside from this relation the two substances have little in common.

From the adrenal-gland of animals there may be prepared *adrenalin* — one of the most powerful agents of the surgeon for preventing bleeding during an operation. Soon after its discovery its composition was investigated and the German, Stolz, succeeded in synthesizing it. This synthetic product is today on the market, sometimes called suprarenalin. It raises the blood-pressure and contracts the blood vessels. The surgeon injects it locally into the tissues when he wishes to reduce the circulation of blood near the point of operation.

For the same purpose also there is used the strange drug, *cocain*, an alkaloid from the leaves of the coca-bush, which grows over a large area of South America. The cocain is an active anæsthetic, used by injection or by painting it on the mucus membrane, to reduce sensitiveness to pain, especially in eye operations.

It also has action on the brain giving rise to certain hallucinations removing the sensations of hunger and thirst, fatigue and sadness. Coca leaves are chewed by the natives in South America and cocain salts are misused like morphin salts by people who have acquired a habit for the poisonous effects of the drug. Cocain, like adrenalin, contracts the blood vessels and raises the blood-pressure. It is commonly used with the addition of a trace of adrenalin, to make bloodless surgical operations and to reduce their pain. Cocain, however, is extremely poisonous and also it causes local irritations where injected. So a search has been made to find some less dangerous agent to replace it. In 1915 Einhorn discovered a preparation, novocain, a derivative of benzoic acid, which is the best drug yet found for this work. It is about seven times less poisonous than cocain and it lacks its irritating properties. Novocain also is used with a trace of adrenalin added. It is considered the best known agent for local narcosis and its use has been a great addition to the technique of surgery. It is made nowadays in factory quantities. Incidentally it might be added here that chloroform, iodoform and bromoform are now made electrolytically on a large scale.

Very great progress had been made in the field of sleeping powders. The sleep-producing agents *sulfonal*, *trional* and *tetronal*, and particularly Emil Fisher's compound, *veronal*, and a related chemical, *luminal*, are all made today on a technical scale. They have become indispensable. The two first named are made from alcohol, the third from acetone, which is made to react with mercaptan, an extremely evil-odored substance related to the gas, hydrogen sulfide, of an odor like rotten eggs. Mercaptan is known in Sweden as an undesirable

by-product of the sulfite-cellulose industry. To get rid of the penetrating odor of this substance the sulfite-process factories are forced to erect very tall chimneys, in order that these shall lead the noxious gases into upper-air currents. Many people can remember how the air of Stockholm city, once about twenty years ago, was for three days tainted with this substance. The meteorologists were consulted by the newspaper reporters and these scientists demonstrated that an almost complete calm had prevailed during the three days in question, so that the smoke of the city had not been carried away. They further said that the odor must be the "city's own smell!" Their answer displayed humor mixed with spite. The actual fact was as follows: A Stockholm scientist conceived the idea of testing methods for getting rid of the annoying odor which was being let loose from the stacks of a paper-mill in a near-by city. To study these methods he decided to make some experiments regarding the properties of the substance mercaptan of which he had a supply sent him in a bottle. When his investigations were done he wanted to get rid of the odorous bottle and contents so he gave it to an errand-boy, who, one dark morning, unobserved, cast the bottle into an arm of the Baltic near the city. The effect was magnificent! It was a considerable time before the scientist let the true story be made known.

A similar fate fell to the lot of the district surrounding a factory where three of the above-named soporifics, themselves completely odorless, were first made on a large scale. The difference was that while the inhabitants of Stockholm suffered only a three day test of their sense of smell, the environs of the factory were continually enveloped in the strong stench — until the police resolutely closed the factory. Then this factory was forced to move to Luneburg-Heide, a deserted heath, where the work could proceed in peace. Modernly an apparatus has been devised such that the mercaptan does not escape in noticeable amount.

The last two soporifics named above have come to replace

almost wholly the previous use of morphine, partly because of their freedom from the dangerous and undesirable after-effects of morphine; partly, and this is yet more important — because the patient does not have, to any extent, the horrible craving for the drug which generally follows the use of morphine. Sulfonal is slow-acting, because of its low water solubility; also dangerous side-effects have been noted in its use. Trional is considerably better, but is surpassed by tetronal and still more by *veronal-sodium*, and by *luminal*, which latter therefore are widely used by both physician and patient.

For a long time the simpler compounds of arsenic, especially arsenious acid, have been used in fighting pernicious anæmia, certain skin diseases and those diseases, especially sleeping sickness, which are caused by trypanosomes. It was next sought to make arsenic-containing substances of organic character, in order if possible to discover more powerful agents, which at the same time should not be so poisonous, and therefore not so dangerous to the patient. The German, Blumenthal, in 1902, introduced into therapy such a substance called *atoxyl*. It had been discovered as early as 1863, when the Frenchman, Béchamp, heated together anilin and arsenic acid. On investigation it was shown to be a sodium salt of a complex arsenic-containing acid. It was used successfully by the English worker, Thomas, in 1905 in fighting the tropical diseases of humans caused by trypanosomes and similar organisms, among these diseases being malaria, and the sleeping sickness; and it was also used by the famous German physician, Koch, (in 1907) to fight the cattle-plague then prevalent in South Africa. Furthermore this drug was found to be active against pernicious anaemia, and also quite active against syphilis. However, it had the very great disadvantage that it endangered the eyesight and that not infrequently blindness resulted.

Ehrlich, therefore, in his laboratory for chemotherapy at Frankfort, Germany, sought to find new organic arsenic compounds, which might be better than atoxyl. One of his pupils, the Japanese, Hata, tested the compound resulting from the

606th of Ehrlich's experiments and he found it to have the desired properties. At first Hata called it 606, later salvarsan, and today the names arsenol and *arsphenamine* are also applied. Since then many new similar agents have been synthesized, such as *neo-arsphenamine*, *sulf-arsphenamine*, and many others. In France, at the Pasteur Institute in Paris, similar studies are carried on, and in America at a number of centers, among these the Rockefeller Institute and the Hygienic Laboratory of the Public Health Service at Washington. The arsenical drugs are of great use in fighting diseases of the type of the trypanosome diseases, especially relapsing fever, and also sleeping sickness, malaria and syphilis.

While searching for the drug, 606, Ehrlich found certain dyestuffs, trypan red and trypan blue, containing no arsenic or other metal but only carbon, hydrogen, oxygen and nitrogen. These were somewhat effective in killing trypanosomes. Recently the Bayer Co. in Germany has announced a drug capable of curing sleeping sickness, and probably elaborated from some molecule rather similiar to these dyestuffs. It has been named Bayer 205 and its composition has been kept a secret.

Morgenroth in Berlin has investigated derivatives of quinine which have long since far surpassed that drug itself for fighting malaria. He found in his work a drug called *optochin*, which appears to be particularly active against lung-inflammations such as pneumonia, diseases which have carried off so many people, often at their most useful and productive time of life. Much work remains to be done in this field.

Chemistry has also prepared, for the improvement of hygiene, a great series of powerful antiseptics and disinfection agents. Among these may be named, besides the inorganic products such as hydrogen peroxide and mercuric chloride, called sublimate of mercury — further: lime, and chloride of lime, also the organic chemicals, formalin, phenol (carbolic acid), thymol, lysol and cresol. Also of course there is iodine. The American surgeon, Carrel, and the English chemist, Dakin, during the world-war devised the best yet-known method of keeping

wounds sterile and clean, and for this they used a solution of sodium hypochlorite.[1]

The manufacture of synthetic drugs was first fostered by the great German dyestuff factories as an outlet for some of their by-products. These same factories have also sponsored the preparation of the different antitoxins which are counter-poisons against the bacteria and the poisons of the bacteria which cause the commonest and the most dangerous of the diseases. The antitoxins are produced in the bodies of animals as a result of chemical reactions which are not yet fully understood. (Tr. Note: Professor Arrhenius has been one of the leaders in this latter field of study — called *Immunochemistry*).

From the foregoing chapter one can clearly see that the chemical industries not only have given us the finest of colors and perfumes for the satisfaction of the esthetic needs of man, but still better, they have greatly contributed to our arsenal of medicines wherewith the battle against sickness and misery are waged. Over 5,000 synthetic drugs have been made, but of course only a few of these come to be accepted in regular practice. There seems little doubt but that today only the foundations have been laid, and that there are possibilities of development in this field which shall bring power, health and success to future generations to a degree which we can hardly now imagine.

[1] Except in the case of adrenalin the chemical composition of the secretions, or *hormones*, which are poured into the blood by the various ductless glands and which act as messengers to produce effects in various organs of the body, is unknown. But today one of these secretions is prepared in large quantities from the pancreas-glands of various animals, and is in use for fighting the disease known as diabetes. This gland-product is called *insulin* or *iletin*. Doubtless its structure will soon be made known to the chemists who are studying it, and then perhaps it will be possible to synthesize it and so bring about another triumph for chemical science in the service of medicine. Insulin was discovered by Banting and Best in the laboratory of MacLeod at Toronto.

Chapter XIII

CELLULOSE AND RUBBER

Cellulose is a carbohydrate. That is to say it is a compound of carbon with oxygen and hydrogen, in which the two latter constituents are present in the same ratio as they are in water, one atom of oxygen to two atoms of hydrogen. The chemical formula of cellulose is $(C_6H_{10}O_5)_n$, where n is an unknown number. We know the percentage composition of cellulose but we are still in the dark as to the size of its molecules. Since cellulose and its compounds do not form well defined crystals, but possess colloidal properties, it is believed that the number *n* is very high, so that the molecular weight is very great.

These colloidal properties of cellulose and its compounds account for its wide-spread usefulness, just as the colloidal condition of the silicates after they have been melted lends them their high value. Cellulose compounds differ principally from the silicates in certain physical properties for they have very high plasticity, a property very important for many of the uses of cellulose. Cellulose has another very valuable property, namely that it is not readily attacked by the oxygen of the air nor by water.

Cellulose forms the membranes of plant cells. Pure cellulose occurs as cotton-fiber, after other substances in the cotton have been removed by the use of alkalies, acids and bleaches. Wood is one of the chief sources of cellulose because of its high content of that material. It is used especially in paper making. Paper was formerly made from rags, and some high grade writing papers still contain them, (linen papers, for example). But as these materials became scarce it was found that they could be mixed with "mechanical pulp," which was made by

grinding wood on rotating mill-stones. This use of wood pulp was discovered in 1846 by Voelter and was in use in Sweden in 1850. This pulp was always used as an added material in paper making; it cannot be used alone because the fibers are broken and shortened as a result of the grinding. If the wood was steamed before grinding a pulp could be made that can be worked up by itself into pasteboard or brown wrapping paper. It was soon sought to separate the wood fibers by some chemical means, in order not to tear and grind them. Wood consists of cellulose, lignin and various resinous bodies. To free the cellulose from the other substances, in a process developed about 1870, wood-chips were boiled with 20–25% sodium hydroxide. But later it was found that a stronger, more durable goods resulted if the alkaline solution contained sodium sulfide, which latter was prepared from sodium sulfate. The product obtained in this was called sulfate mass. Another method was worked out in 1874 by K. D. Ekman at a Swedish factory. In this method the wood was boiled at 140–106° C. with a solution of acid magnesium sulfite. The lignins and other by-products were dissolved out and pure cellulose remained behind. In the seventies, Alex. Mitscherlich made a change in the process and instead of using magnesium-sulfite liquor, prepared from dolomite, he used acid magnesium or calcium sulfites or calcium sulfite solutions prepared from limestone. This process is still used today, with a chamber-apparatus invented by E. Partington. The mass so obtained is called sulfite-cellulose.

Before the cellulose mass is worked up into paper it is bleached, washed and, if desired, suitable dyes are added. Then it is beaten up into a paste with water and led onto an endless wire netting or screen running on rollers. Here most of the water runs off; the last roller is heated by steam to drive off the remaining water. Finally the paper, according to its destiny, is cut or handled in a suitable way.

When the pulp is to be prepared by a chemical rather than a mechanical process there are many by-products to be removed

which otherwise would be very troublesome. Wood-scrap can be oxidized to oxalic acid by heating it with alkali. Most of the market-supply of this acid is made in this way. In Sweden the waste wood is commonly subjected to dry distillation, or else is used as a fuel. Charcoal is obtained as a solid residue in the dry distillation, while gases and a watery liquid pass off. These contain acetic acid, acetone and methanol as chief constituents. These important chemicals are chiefly made in this way at present. It is possible that some day these methods will be superseded in part by the preparation of acetic acid and of acetone from acetylene made from carbide. The acetylene can easily be converted into acetaldehyde and thence to the other chemicals. Since wood distillation is the main source of methanol, however, and since this is used in many chemical processes, the demand for this chemical will probably keep alive the distillation process.

Most of the by-products are found in the liquors remaining after the chemical treatment of wood pulp. To make use of the many organic substances contained in sulfite-liquors Strehlenert has suggested the preparation of a fuel from them, called "sulfite coal." The mass is heated at 170–190° C. in an autoclave while air is passed in and the calcium sulfite oxidizes to calcium sulfate; sulfurous acid and hydrogen sulfide pass off and can be made of use. Water is also driven off and there remains a solid mass, the combustible "sulfite coal." Industrial alcohol can also be obtained from sulfite liquor and is then called "sulfite spirit." The liquor is neutralized with potassium hydroxide, the nutrient materials needed by yeast are added, and then it is fermented. The alcohol formed from the sugars contained in the original liquors is distilled off. However, in this way only 5% of the total organic substances present in the sulfite liquor can be made use of. One liter of spirit could be made from the liquor from each 20 grams of pulp. This process can afford a considerable amount of alcohol. In Germany, for example, in 1909, 600,000 tons of sulfite-pulp was made, so from the liquors 30 million liters of alcohol could have

been obtained. In the United States in 1920, 3,800,000 tons of wood pulp were made; 40% was mechanical pulp, 40% sulfite pulp and the remainder soda pulp and sulfate pulp. The total value was 276 million dollars.

Cellulose is the raw material for a large number of chemically prepared substances. The most important of these is nitrocellulose. In 1846 Schönbein produced "gun-cotton" by nitrating cellulose (cotton) with a mixture of nitric and sulfuric acids. Cotton residues are used mostly, and in the war period even wood cellulose was used. On ignition the gun-cotton burns without explosion. The explosion occurs by shock, and this is generally supplied by the detonation of mercury fulminate. A great volume of gas is formed in the explosion and contains nitrogen, carbon dioxide, carbon monoxide and water vapor. The gun-cotton can be exploded when wet and this makes it an important agent for blasting under water. If gun-cotton is dissolved in acetone or a mixture of alcohol, and ether, when the solvent is evaporated off it becomes a colloidal mass. This was the first smokeless powder.

Alfred Nobel, the great leader in investigations of explosive technique, found in 1863 a process for making nitroglycerine in large quantities. This explosive had been discovered by the Italian, Sobrero, in 1846. In 1864 Nobel found that the nitroglycerine could be exploded with the use of an ignitor of mercury fulminate. But the unmixed liquid nitroglycerine was very dangerous to handle so he mixed it with Fuller's earth which absorbs it and forms a plastic mass. Such a mass was *dynamite*. It has found widespread usage. Nowadays sawdust takes the place of the Fuller's earth as absorbent.

Later Nobel mixed nitroglycerine with gun-cotton and so he obtained a very powerful gelatinized explosive called blasting gelatine. This has found considerable use because of the comparatively low degree of danger involved in handling it. In England this material was given the name cordite and was prepared by mixing 65% gun-cotton, 30% nitroglycerine and 5% vaseline. To this mixture was added a little acetone and

the plastic mass was then pressed out into thread or "cord"; hence the name, *cordite*. After the added acetone had evaporated there remained a horn-like mass, insensitive to shock, so that it could be handled with little danger. This discovery of Nobel's that an explosive when dissolved in another explosive "gelatinized" and then became safe to handle has been of great practical importance and such gelatinized explosives now play the main roll of propellant explosive-charge for projectiles.

The lower nitrates of cellulose when dissolved in alcohol and ether give a liquid called *collodion*, which dries in a film on evaporation of the solvent. Collodion was discovered by the American, Maynard, in 1847. It has been used in surgery to cover open wounds after operation, and also it was formerly used in photography; the "collodion plate method" was once used almost exclusively. The type of nitrocellulose from which collodion is made is called collodion cotton and this is also the source of celluloid and of some kinds of artificial silk.

In 1869 the American, Hyatt, discovered that collodion cotton dissolves in camphor, giving a gelatinous mass, plastic when warm, horn-like on cooling. This mass was called *celluloid* and is made and used in great quantities. Tissue paper is used as the source of cellulose for this material. This is nitrated in a mixture of equal parts of sulfuric and nitric acids. After the nitration it is ground and washed, then the water is pressed out and the damp mass is mixed with half as much camphor. The water is then wholly removed, and if desired a dye is now added, then it is subjected to heavy pressure at 130°C. The cellulose completely dissolves in the camphor. The final drying is carried out in a vacuum drying oven. In another process one and one-third volume of ether or of methyl alcohol is added to the mass, and then it becomes plastic and can be worked at ordinary temperatures. Kneading follows in a closed apparatus until the mass is uniform, and then it can be moulded. Celluloid is adapted to the manufacture of all sorts of objects. A solution of it in ether-alcohol,

or in amyl or ethyl acetate makes an excellent varnish called japan-lac and used for coating all sorts of surfaces such as wood, metal, paper or cloth, giving a thin transparent coat which may be cleaned with water and soap. Pergamoid is a gelatinous solution of cellulose of any color, used for the same purpose. A great disadvantage in the use of celluloid is its inflammability. At 150° C. it catches fire and burns fiercely with a camphor odor. In particular, bad accidents have been caused by the firing of the film used in motion picture machines. Today it is largely replaced by acetyl-cellulose, which is not inflammable, and will be described below.

If paper is dipped in sulfuric acid for a short time the cellulose changes into a gelatinous mass called *amygdaloid*, which fills the pores of the paper and after washing and drying, renders it impermeable to water. This is called *parchment paper*. If many sheets of this paper are pressed together, one obtains a material called in England hard-fiber, which is used for the manufacture of trunks, hand-baggage, etc. This also has considerable use as an electrical insulator.

A parchment paper can also be made by the action of a very dilute solution of zinc chloride on cellulose or paper. The name *amyloid* is given to this, because like starch, it can be turned blue by iodine, (the Latin for starch is "amylum"). For this reason zinc chloride and iodine are used as reagents for the recognition of cellulose, and especially for the recognition of minute quantities of it under the microscope.

Strong hydrochloric acid decomposes cellulose very rapidly, so that acid is used as a reagent to distinguish wool and silk from cotton or artificial silk — for example in mixed cloths. In this connection it may be said that alkalies act on fibers from animal sources, wool and silk, much more powerfully than upon cellulose. But if cotton is dipped into concentrated sodium hydroxide solution a salt is formed made up of one molecule of sodium hydroxide with two of cellulose $(C_6H_{10}O_5)_n$. Cellulose is an amphoteric substance and can form salts with both acids and bases. Other carbohydrates such as the sugars,

and also the higher alcohols such as glycerine and erythrite possess this ability to form salt-like compounds with both acids and bases. (For example, nitro-glycerine is glycerol tri-nitrate). In the case of cotton, the fiber swells on taking up sodium hydroxide and though naturally curled, straightens out. Fibers draw together and shrink lengthwise, taking on a shining lustre rather like silk. This results from the parallel position of the fibers. The luster remains when the sodium hydroxide has been washed away, and the durability of the fiber has been increased by the process; furthermore, it will take up dyes well. The fibers stretch again, but their parallel position remains. This process was discovered by an Englishman, Mercer, in 1844 and is known as *mercerization* of cotton. For a long time the process was not used commercially, until a plant at Krefeld, Germany, took it up and treated both yarn and cloth in this way. The spinning hinders shrinking of the fiber. The mercerization can be controlled so that only part of the fabric is treated while the rest remains unchanged. The goods then possess a crepe-like appearance.

A characteristic solvent for cellulose is copper-oxide-ammonia, that is to say, a solution of copper oxide in ammonia water. Such a cellulose solution is used to coat paper. The coated paper is then let lie in the sun and the ammonia volatilizes, leaving the paper with a malachite-green, waterproof coat. If it is now dipped in acids the copper salts are dissolved out and a pure cellulose surface remains. This is called Willesden paper. Other objects are also so coated and known as Willesden ware.

A concentrated solution of zinc chloride dissolves cellulose and forms a thick syrupy liquid. If this is run as a thin stream into alcohol a thread is formed. Dried and carbonized this thread was formerly used for the electric glow-filament in electric-light bulbs, but has now been very largely replaced by tungsten filaments.

Cellulose reacts with carbon disulfide to give a characteristic product called cellulose xanthate. This is soluble in water.

This solution is gelatinized by salts or by alcohol or even on long standing by itself, in which case it decomposes so that free cellulose precipitates as a plastic mass, which has been used for moulding various objects.

In the manufacture of *artificial silk* solutions of collodion cotton or of cellulose are employed. They are pressed through very fine openings into a liquid where they form very thin threads. This industry was started by a French engineer, H. de Chardonnet. He let a solution of collodion cotton in alcohol-ether mixture, flow as the finest of streams into water. The water dissolved the alcohol and ether and left the collodion cotton thread. However, the great inflammability of this product was dangerous. This brought about a change in the method of manufacture whereby the thread was treated with a solution of ammonium sulfhydrate, NH_4SH. This chemical decomposed the nitrate, and the threads again became pure cellulose. This process was called "denitrification." The fiber was then bleached, dyed and washed with acetic acid and soap solutions and thus there was made an artificial silk which had softness and "rustle," (the characteristic sound heard when silk is rubbed on silk) — while chemically it was still cotton, and quite different from the silk-worm's product.

Artificial silk is also made with the use of the solution of cellulose in copper oxide ammonia. Here the threads are formed by pressing out into a dilute acid solution, which dissolves the copper oxide and the ammonia and leaves pure cellulose. In Germany the product is known as "luster-cloth," "Glanz-stoff."

A cellulose xanthate solution can also be used in the preparation of artificial silk. This type goes to the market as "Viscose." It is pressed out in threads into a solution of ammonium chloride. The carbon disulfide and the sodium hydroxide are removed and pure cellulose fibers remain. This latter method was discovered by two Englishmen, Cross and Bevan. The product is called viscose-silk and somewhat surpasses the other two artificial silk products in luster, durability and ability to

PLATE X

Courtesy of the I. E. duPont de Nemours Co.

THE COMFORT CHEMISTRY OF CELLULOSE.

Besides paper and artificial silk, cellulose provides us with artificial ivory. Tissue paper is nitrated or an acetyl cellulose made from it. From the nitro or acetyl cellulose with the aid of organic solvents plastics are prepared which are moulded under high pressure. The objects here shown are toilet articles made of Ivory Pyralin.

take a dye uniformly. There is still another artificial silk made from cellulose acetate (see below), and this bids fair to be still better.

The artificial silks have a higher luster than has natural silk, while they cost but half as much. However, they cannot truly replace the natural silk. The fibers of natural silk are finer and the cloth lighter than the artificial silk cloth, while the latter is not very durable, especially in damp climates. The artificial silk is used in large amount for decorative purposes, lace-work, draperies and furnishings, also for clothing, and even artificial human hair and horse hair are made from it, as well as gas mantles for the Welsbach light. The world production in 1922 was about 36,000,000 kilos of which the United States produced 10,600,000 kilos, next in order were England, Germany, France, Belgium and Italy. In 1921 the United States imported about 130,000,000 kilos of unmanufactured natural silk.

We have seen that as a result of the dangerous inflammability of celluloid bad accidents and fires often resulted. Unfortunately the dangerous properties cannot be removed from this product by treating it with sulfhydrate, as can be done in the case of cellulose nitrate used for artificial silk. But a substitute has been found. The great inflammability of the celluloid was due to the content of cellulose nitrate, just as that of black powder is due to potassium nitrate. We might therefore imagine that another salt, or in other words another ester, might possess all the good properties of the nitrate but lack its inflammability and explosiveness. In place of the highest nitrate of cotton, $C_6H_7O_6(NO_3)_3$, another ester can be prepared, the acetic acid ester, $C_6H_7O_2(CH_3CO_2)_3$, cellulose triacetate. The famous French chemist, Schützenberger, prepared this chemical in 1869, by heating together cellulose, (cotton or filter paper), with acetic anhydride. The acetate thus made dissolved in camphor or other suitable agent, possessed all the good properties of a celluloid without being inflammable. The acetate is called *cellite;* its camphor solution, the substitute for

celluloid, is known as *sikoid*, and this was first made by the German, Arthur Eichengrün. Sikoid is soluble in chloroform or in acetone. It is chiefly manufactured by the Society Industrielle de Celluloide in Paris and is used for non-inflammable moving-picture film, etc. The importance of the industry can be seen from the 1911 production which was 100 million meters of film. The continual increase of popularity of the cinema has surely increased the figures greatly since the war.

Sikoid is just as useful as celluloid, and can even replace rubber and gutta-percha in many cases. Artificial bristles and horse hair are made from it, and from these, as well as from artificial silks ladies' hats are made. Sikoid solutions are used as varnishes for paper and metal objects, and it is quite largely used for varnishing the wing surface of airplanes. These are not only made water-tight but are made stiff and smooth, by the use of this coating material. It is an excellent electric insulator, not only because of its high resistance but also on account of its low dielectric constant. A good artificial silk can be made from the cellite, cellulose acetate, by making a thick syrup of it with chloroform and then pressing it out into threads. The Bayer Company makes "Baykoyarn" dresses and gowns from cellite. For this purpose cotton fibers are covered with a cellite solution in which are suspended silvery or gilt metal flakes. A silvered or gilded yarn is obtained which will not blacken because of the coating of cellite. Such yarns can be made in all the known colors, so that very interesting color effects can be obtained.

In recent years non-inflammable film has also been made from viscose. The viscose solution is pressed through a slit of adjustable width, about a meter and a half long and is led into a fluid which precipitates the cellulose xanthate as a solid. When first formed it holds 80% water. It is carefully washed and dried. It then shrinks to one-third size, so that it is finally less than a meter wide. This method was devised by the Soc. Français de la Viscose under the direction of L. Naudin and J. E. Brandenburger.

A colloidal substance which has immense commercial value is *rubber*. The world consumption in 1921 was 285,000 tons (1920, 343,000 tons). The users in 1920 were the United States, 24,800 tons; Britain, 56000; France, 16,000; Italy, 7,000; Japan, 7,000; Australia, 6,000; Canada, 11,000.[1] Chemical industry has before it no problem of greater economic importance than the rubber problem. Rubber is made from the milky juice of many tropical plants, especially of such families as the Euphorbaceae, Certocarpaceae and Apocyanaceae. In the early days Brazil furnished half of all the rubber, and the best "para" rubber was made from the juice of the plant, *Hevea braziliensis*. If rubber is treated with sulfur chloride at ordinary temperatures, or with sulfur at 160–180 it combines with the sulfur, and the nature of the rubber is much changed; it becomes "vulcanized." The vulcanized rubber can better withstand mechanical, thermal and chemical attack, than can unvulcanized raw rubber. With higher sulfur content rubber hardens and is then called ebonite or hard rubber. With age, rubber hardens of itself. This latter phenomenon is explained as due to combination of the rubber molecule $(C_5H_8)_n$ with itself to form higher and higher complexes. The "n" in the formula becomes a greater and greater whole number. There are many ways of regenerating such a hardened rubber. Regenerated rubber can be added in considerable quantity to new rubber before vulcanization, without injury to the product. The most valuable property of rubber is its so-called elasticity — the ease with which it can change its form and then on release of pressure go back to its earlier form.

The same percentage composition as rubber is shown by a certain liquid hydrocarbon, isoprene, C_5H_8, which boils at 37° and also possesses the scientific name of methyl butadiene.

[1] The figure for 1910, world consumption, of rubber was 73,000 tons. The war upset all statistical figures, and a long time must pass before normal production will again result. The statistics, since 1913, cannot be looked upon as normal. The chemical industries at the beginning of war were transformed into factories for the preparation of needed war materials. The re-adjustment after the war has been slow, and is only beginning to approach normal again.

By heating this chemical below 100° it changes over into a rubber-like substance which can be vulcanized. This change can also go on at room temperature, but only very slowly. Various catalysts will speed the change, which consists of a polymerization of the molecules so that $(C_5H_8)_n$ molecules are formed, and n probably becomes a very high number. On the other hand isoprene can be gained from natural rubber by dry distillation of the latter.

The chemistry of rubber was studied for many years by the late Prof. C. Harries of Kiel University and by his pupils. Their researches made possible the artificial preparation of rubber. Such artificial rubber was made in 1919 by two chemists, F. Hoffman and C. Coutelle, at the Eberfeld Co. laboratories. In making synthetic rubber not only isoprene, but two other hydrocarbons also have been used, namely butadiene, a gas at room temperature — it boils at 4° C., and the liquid, dimethyl butadiene, boiling at 69° C. A multitude of objects, tires, electric-cable insulation, and rope have been made from these artificial polymers. The chemicals named are simply kept warm for a long time, and gradually change over into the polymerized form. The objects made from such rubber have been in use for a sufficiently long time to make certain that they are just as useful as ordinary rubber. But the question of price is the deciding factor. Just before the war artificial rubber, without counting in any manufacturing or trade profit, cost $1.44 per kilo. This price might be compared with the cost at that time of "wild" natural rubber, about $1.20 per kilo and with that of the plantation rubber grown since 1900 in great quantities in Java, Sumatra and Ceylon, which at pre-war prices cost from 50–75 cents per kilo. Thus it can be seen that the German chemists did not succeed in underbidding the price of natural rubber, but they did succeed in making it impossible that prices as high as $5–$6 per kilo (as in 1910) need ever again be feared. The threat of synthetic rubber has broken the plantation monopoly. It is to be hoped that some day the chemist can actually underbid the plantations, and so

PLATE XI

Reproduced from Luff's "Rubber."

COLLECTING RUBBER LATEX.

Nature can still produce rubber more cheaply than can man.

free the rich areas which they cover, making them useful again for the growth of food materials.

All the above demonstrates that in recent years it has been the industrial chemist who has led the field in finding new ways to produce useful articles. The system common nowadays in great chemical plants by which the scientists and workmen of the plant work in highly specialized fields has its great advantages but also certain disadvantages. If work in a factory is stopped and its great personnel dispersed, (this can be compared to taking apart the cogwheels of a complicate machine) when the work starts up again it takes a long time before the plant can again attain its former smooth-running condition. A difficulty of this sort was experienced in all the combatant countries during and after the war. The factories for a very long period had to turn their energies to the preparation of war materials, and the ordinary processes of these factories rested. On starting up again after the war a great number of new people had to be engaged while those who remained from pre-war days had lost some of their skill in their special work; a skill which had only been gained by daily practice.

Another difficulty in these big industries is the great secrecy of the processes. The scientifically trained men engaged in research in the plant are wont as a result of their university or institute training to talk of their work with the greatest of freedom among their professional colleagues. By such free intercourse much is gained on all sides. But if these investigators enter the factory they must not discuss what they see, though they are often confronted by new and astounding scientific facts, which, if only available, they know would be of the greatest value in other fields and in advance of science. Many of these scientists come to feel themselves unpleasantly driven and hampered by this policy; they behold in it a passive resistance to the advance of truth and science; they feel themselves called to serve the latter and therefore long to get back to free and open research.

Yet for the most part the multitude of scientific men work-

ing in such plants strive to hold alive an interest in the advance of science. They form societies in which the new results in scientific fields can be presented and discussed, naturally with special regard to how they can be brought into use in technical practice.

Copying the method of the great factories, which was seen to be so successful for producing results under stress of war, in the war years it was sought to organize coalitions of scientists and engineers, with nearly unlimited national backing, both financial and material, to effect discoveries and improvements in phases of war work. It has been asserted that this type of organization has gained the very best results. Now in the post-war days attempts are being made to continue similar organizations for encouragement of the development of mankind's various benefits, though most of these organizations still possess a strong national stamp. It is not to be wondered at that many independent investigators are little of a mind to fall in with such "imperialistic" systems, for these are counter to the spirit of the times.

Chapter XIV

CHEMISTRY AND THE BREAD QUESTION

Living organisms are built up of a few common elements, chiefly carbon, hydrogen, oxygen, nitrogen, with a little phosphorus, sulfur, copper, iron, sodium and magnesium. From these elements there have been attempts to prepare artificially substances corresponding to the nutrient materials made by nature. It must be admitted that the advance upon this road has not been very far. It is quite possible for man to make synthetic carbohydrates and fats and even protein-like substances, which can serve as food materials, but if one tried to make these on a factory scale one comes upon the unsurmountable difficulty of obtaining them at a reasonable price, or in other words with the expenditure of any easily available amount of energy. The animal and plant world supply foodstuffs at so low a cost that the chemist cannot dream of competing with them, not only today but far into the future. The "white powder" of which the great chemist Berthelot dreamed, which was to contain in tiny doses all that was necessary for a day's ration is an unrealizable fantasy on the ground alone that we require very considerable amounts of the three fundamental types of food, fat, carbohydrate and protein, for our daily need. And the matter is complicated by the fact that we also require tiny amounts of very complex food-accessories — the vitamins. We can see how impossible is the proposition of tabloid food.

For a long time men thought that the living cell had a very different way of going about its work from any apparatus or process of the chemist. The deeper, however, that these vital processes are studied the more certain it is that those sharp boundaries which we used to draw between organic and inorganic nature are more apparent than real. Among the indus-

trial processes which have been in use from early antiquity there may be counted fermentation. Sugar by the action of yeast is turned into alcohol and carbon dioxide. This change was long believed to require the action of a living organism, until the great French biochemist, Duclaux, showed that sugar in the presence of any base — that is to say in the presence of the hydroxyl ion — and under the influence of ultraviolet light, always changed to alcohol and carbon dioxide. Later Buchner and Meisenheimer showed that even the ultraviolet light was not necessary to this process, for alcohol was formed when grape sugar was boiled with strong potassium hydroxide. Light is very active and it is indispensable in those processes where it supplies the energy necessary for the change. That it is not needed in the case of alcohol formation is due to the fact that energy is not used up in this latter process but is given off. The most important of all processes of nature go in the opposite way. Sugar and the other carbohydrates in the green plants are produced by the aid of the catalyst, *chlorophyll*, leaf-green, from the carbon dioxide of the air and from water from the soil. In this case a great deal of energy is used up, so the change can take place only in the light, sunlight or electric light, which latter is occasionally made use of in greenhouses. This light-process was first studied by Priestley and has since drawn the attention of many leading scientists. Baeyer claimed that from carbon dioxide and water first oxygen was split off and formaldehyde was formed (H_2COH) and then this was polymerized to glucose ($C_6H_{12}O_6$), or other sugars, or to cellulose.

In recent years the Bohemian, Stoklasa, and the French scientist, D. Berthelot, son of the famous M. Berthelot, have tried to produce this reaction under the influence of ultraviolet light but without the presence of any living organism. Berthelot and his pupil, Gaudechon, in 1910 let the light from a mercury arc-lamp, giving strong ultraviolet radiation, act for twelve hours on a mixture of carbon monoxide and hydrogen and found that formaldehyde was synthesized. They concluded

that water and carbon monoxide result from the influence of radiation on carbonated water and that formaldehyde then forms from the monoxide. Stoklasa and his pupil, Zdobnicky, also in 1910, found that carbon dioxide and hydrogen (in nascent state, such as hydrogen developed from sulfuric acid and zinc) formed formaldehyde and oxygen under the ultraviolet light. In later studies they have tried to prove the formation of formaldehyde and oxygen from carbon dioxide and water under the ultraviolet radiation. By the action of potassium hydroxide on formaldehyde higher carbohydrates can be formed. In 1890 Emil Fischer synthesized fruit-sugar from formaldehyde. In the years 1920–23 an interesting series of researches in this field has come from the laboratory of Prof. E. C. C. Baly at Liverpool. Baly not only obtains sugar and formaldehyde from carbon dioxide and water under the light from a quartz mercury vapor lamp, but also, when nitrites are present in the solution, obtains amines and amino acids. Thus the chemist, without the intervention of living matter, but using the energy of light, is able to take the preliminary steps toward the synthesis of proteins. These attempts to imitate the carbohydrate and protein synthesis in the plant are most interesting, but unfortunately they are not and probably will not be in the future of any great practical feasibility.

So we must concern ourselves rather with problems of changing natural organic substances possessing undesirable taste, or such as do not at present serve as food, into useful foods, or we must try to increase the production of life-stuffs in nature by more intensive cultivation. We have made some progress in the first of these fields, for we make use today of the Sabatier method of hardening fats with nickel and hydrogen. The process of hydrogenation can be stopped at any desired stage and thus fats of any degree of hardness can be obtained, from fluid oils to solid fats. Among the glycerol esters of fatty acids that occur in nature, and make up the main bulk of the natural fats, oleic and butyric esters are liquid at ordinary temperatures. Palmetic ester melts at about 62° C. and stearic

ester at about 71° C. Great quantities of liquid fats are thus worked over. Most of these are derived from the plant kingdom, especially palm oil, but in part also oils from the animal kingdom, such as cod liver oil, are used. Useful food-fats of the consistency of butter are obtained. The preparation of artificial butter, "margarine," from less valuable fats by purifying them and suitably mixing and churning them with milk, is quite a well-known process. Margarine is a cheap butter substitute but as a fat is just as nutritious. However, its content of the vitamins and similiar necessary food-factors will depend on the amount of milk used. In the same way fat cheese may be prepared by emulsifying renovated, cheap fats with skim-milk and then curdling the emulsion. The fat-needs of man can thus be appeased in a less expensive way than by the use of natural animal fats such as butter and lard. The chemistry of fats was made clear in 1810–13 by Chevreul. He showed that they were glycerol esters of fatty acids, chiefly stearic, palmetic, and oleic acids.

The chemistry of the sugars was clarified by Emil Fischer in the years between 1890 and 1902. Besides natural sugars, such as grape sugar and fruit sugar, he also succeeded in preparing synthetically many sugars not as yet found in nature. Such sugars have no practical importance today. On the other hand there is the greatest practical value in the process by which starch sugar (glucose) or starch syrup (corn syrup) may be prepared from starch-meal (commonly from potato or corn-starch). The starch, stirred up with water to a thin paste is run in a thin stream into dilute sulfuric acid and then heated in an autoclave at two atmospheres pressure. The liquid is freed from sulfuric acid by neutralization with lime and is filtered from the gypsum so formed and then evaporated. The final product consists of a mixture of grape sugar and dextrin with a moisture content of 17%. In syrup the sugar and dextrin are present in about equal amount while in the starch sugar which is boiled longer in manufacture, the ratio of sugar to dextrin is about two to one. Both these preparations have a consider-

able market (for example they are used in the manufacture of candy and of marmelade). The hydrolysis of cornstarch may also be brought about by hydrochloric acid.

Plant-eating animals can make use of the cellulose in the plant. They do this by the aid of bacteria living in their alimentary canal. But to man cellulose is not a food. As cellulose is much cheaper than other carbohydrates, methods for transforming it to sugar become of importance. This problem is partly solved, but not in a way leading at present to commercially satisfactory results.

In the field of the proteins also Fischer made a long series of important researches. These studies were never completed, but the nature of the proteins had been determined. They are condensed amino-acids. These highly complex bodies result from the union of many simple amino-acids with the splitting off of water, just as one can get cane-sugar by uniting grape-sugar with fructose with the splitting off of a molecule of water. If an animal eats a protein food, this is decomposed in the alimentary canal under the action of "proteolytic" enzymes into simple amino-acids which may then be built up again into body protein after absorption. Under the influence of enzymes in the body-fluids they may again form proteins, but this time those which are characteristic of the given animal. It has been found in experiments upon mice that the protein-needs of animals can be fully covered by using as food-stuffs the same amino-acids as those which are formed in the intestine from the protein foods normally eaten. The cost, however, is much greater than the cost of natural protein food, so these researches have not as yet given promise of great economic value. Among such studies in metabolism may be mentioned those of Henriques, the Dane, and of the Americans, Osborne and Mendel.

In order to increase our supplies of nutrient materials for man and for domestic animals the simplest way is to increase the production on the soil, both by more intensive cultivation and by the lavish use of artificial manures. The very oldest writers

— Virgilius, Pliny the Elder, in his Naturalis historia (23–79 A.D.) and especially M. Porcus Cato in his textbook of agriculture, "De Re rustica," as well as Columella, of Nero's time, in his *Rei rusticae libri XII* emphasized the great importance of dunging the fields. Naturally at that time they had only natural fertilizers. Also in the writings of the other highly civilized peoples of the time, the Egyptians, Hindus, and Chinese, we find this same emphasis. The first who seems to have had any idea of the roll of salts in the soil and of the depletion of that soil by the action of water in washing away salts was the brilliant Palissy, (1510–1589). About 200 years later the Englishman, Jethro Tull, the inventor of the first planting machine, taught that the fruitfulness of the soil could be increased by loosening it, but he claimed that not only the organic but also the inorganic parts of the plant originated from the water. This teaching was also upheld by the Upsala professor, Wallerius, whose book, "The Chemical Basis of Agriculture" (1761), is the oldest textbook of agricultural chemistry. Davy, (1778–1829) and Berzelius, (1779–1848) were both very active in this field. The Geneva professor, de Saussure, (1767–1845), insisted that salts must be of importance in the nutrition of plants. He considered leaf-mould and humus to be important fertilizer materials, and this teaching was taken up by the prominent agronomist, Thaer, (1752–1828), but the latter denied the importance of salts as plant foods. The great Leibig (1803–1873), was the first to bring Palissy's teaching into prominence by his book "Die Organische Chemie in ihrer Anwendung auf Agriculture and Physiologie," (1840). Yet even *he* undervalued the importance of humus, which is chiefly due to its nitrogen content. Finally a full knowledge of the nitrogen need of plants was arrived at, thanks to the work of the Frenchman, Boussingault, (1802–1887), and of the Englishmen, Lawes (1814–1900) and Gilbert (1817–1902).

Many researches have been made since that time with regard to the nutrition of plants. The complicated mechanism has been made more and more clear. Agricultural-chemical

experimental stations have been erected for such studies; the first by Boussingault in 1840 at Pechelbronn in Alsace, followed shortly by that of Lawes, at Rothamsted near London. By 1901 there were seventy such stations in Germany alone. In 1887 an important advance was made by Hellriegel (1831–1895) and Willfarth in their discovery that leguminous plants, by the aid of nodules of bacteria living on their roots, take nitrogen from the air and so increase the nitrogen of the soil upon which they are grown. According to Frank and others the conifers also appear to possess this property. These discoveries furnished an explanation for the methods of "green-fertilizing," known and used by ancient peoples. Later it was found that the bacillus alone, without the presence of the leguminous plants or other "host," can carry nitrogen of the air into the soil.

We have spoken of the importance of bacteria in fertilizing the soil in connection with the fixing of nitrogen. The ability of bacteria to form ammonia and nitrogen is also of importance. The proteins which gather in the soil on the decay of plant and animal residues are decomposed by putrefactive and ammonia-forming bacteria. The end-products of such a decomposition are hydrogen, nitrogen, methane, hydrogen sulfide, carbon dioxide and ammonia gases, which rapidly pass off to the atmosphere. Of these materials the carbon dioxide is of importance because of its activity in weathering minerals, and setting free the mineral foods of the plant. The nitrite and nitrate bacteria also need such foods. The ammonia is most important of all. This generally cannot be used by the plants without first being changed to nitrate by oxidation. According to the investigations of Winogradski this oxidation occurs in two stages. First the nitrite bacteria form nitrous acid, then this is oxidized to nitric acid by the nitrate bacteria, and then the acid becomes bound to the alkali and lime present in the soil. These bacteria cannot endure the presence of free acid—that is why it is so necessary to have lime in the soil. Again nitrites and nitrates in the presence of air and of large amounts

of organic substances are converted into free nitrogen by the denitrifying bacteria. Hence fresh stable-manure can lessen the fertility of damp soil. Before such fertilizer is spread on the fields it is let "burn" as it is called. This must take place at low temperature to prevent loss by oxidation and it is controlled by stacking the manure so that the entry of air is lessened. The very high content of bacteria in stable dung together with its content of straw, valuable in making the soil of the right consistency, causes such fertilizer to possess a value not due to its mineral bodies alone.

Each crop takes from the earth the ash of the plant as well as a considerable amount of organic stuff. The soil is thus made poorer in mineral matter, necessary to the maintenance of the plants. Researches with scientific accuracy in proof of this fact have been carried on for the longest time at Rothamsted. On unfertilized soil the yield during the three twenty-year periods, 1852–71, 1872–91, 1892–1911, fell from a mean value of 18 in the first period to 11.9 and finally to 4.4 units per unit area per year. From another field where the minerals carried away from the soil were regularly replaced there were supplied in the same periods 43.4, 44 and 39.8 units per unit area and year. In the latter case the yield remained practically unchanged. Where no provision is made to replace the mineral stuffs taken out by the crops, many fields are ruined. Farms in the United States which gave splendid yields in their first years of cultivation were worth nothing in the later years of their use, because the necessity of replenishing the soil was not understood. Their occupants have sought new rich soils in the West and in Western Canada. In their first years these new fields give large crops, just as would well cultivated and well fertilized soil. This economic factor has probably been of great importance as an impetus to the settlement of new regions and in the dwindling in population of some of the earliest-settled rural regions of the United States, such as the hill-farms of New England. The soils in Russia, famous for their fertility and known as "Black Earth," black because of their

content of humus, do not yield as large crops as do the well-tilled and fertilized fields of Central Europe.

Different plants deplete the soil differently. The common grains take annually the following average amounts per unit area. Wheat, about 70 kilos of N, 30 kilos of P, 58 kilos of K, 15 kilos of lime. Rye, about the same. Barley, a little less N. Oats, 58 kilos of N, 25 kilos of P, 90 kilos of K, and 25 kilos of Ca. Field-peas use as much P and K as the oats, but twice as much N and three times as much Ca. Potatoes use about three times as much K as wheat. Most root crops use much more. Thus, beets use 160 kilos of N, 60 kilos of P and 222 kilos of K, 110 kilos of Ca. Meadow hay takes a little more N from the soil than does wheat, twice as much K and three and a half times as much Ca. These figures are for well-cultivated soil in the climate of South Sweden. The amount of salts taken from the soil is naturally nearly in proportion to the crop, so it varies from year to year and from field to field. (The unit is the *hectare* = 2.47 acres.)

The salts which are removed from the soil by the plants are mainly nitrates, phosphates, potassium salts and calcium salts. To a lesser degree salts of magnesium, iron and sodium are removed, the last named especially by those plants growing on the ocean beaches or originating from there. Soils often possess insufficient amounts of iron, sodium and magnesium. Magnesium can be replaced in the form of common potash fertilizers such as kainite or carnallite. If the soil is too acid, lime must be added to aid in saltpeter formation. It is not considered equal to the artificial fertilizers but as a soil-bettering material it is somewhat useful, for it is often available near at hand, at marl pits, etc. It is present in various artificial manures, such as calcium nitrate, calcium nitride and bone meal, in superphosphate and in Thomas slag.

The various artificial fertilizers belong to three main classes according to whether nitrogen, phosphorus or potassium is the principal constituent. A very useful economy in nitrogen fertilizers can be made by growing leguminous plants as green

fertilizers. Alfalfa or lupine are often used. Even clover and field peas, with removal of the above-ground portion of the crop, give some valuable nitrogen to the soil from the root system and the straw which remains in the field. If the leguminous crops are used for fodder for cattle, part of the nitrogen can be returned to the soil as animal fertilizer. Such a slow increase cannot take the place of direct nitrogen fertilization. Formerly the most important of such fertilizers was *ammonium sulfate*, a by-product at all gas works. About one-half percent of the coal used for gas is recovered as ammonium sulfate. Theoretically we should be able to get from this source twelve times this amount. When ammonium sulfate is added to the soil it is converted by the action of the lime present into ammonium carbonate, which is absorbed while the calcium sulfate, thus formed, washes out with the rains. This process decreases the lime content of the soil. Another very important nitrogen fertilizer is Chile saltpeter, or *sodium nitrate*. This also combines with the lime of the soil and depletes it. The sodium carbonate formed causes a silting up of the finer humus and soil particles so that these seep down to deeper layers, which thus become less permeable to water. The fertility of the upper layers decrease. Ammonium sulfate produces rather similar results. Care must be taken therefore that these salts are not used in excess.

In recent years atmospheric nitrogen has been "fixed" for the preparation of fertilizers. The three processes have been discussed in another chapter — the Birkland and Eyde, the Cyanamide, (Frank and Caro), and the Haber process. The nitric acid made by the first named of these processes can be combined with lime to form *lime saltpeter*. This takes up moisture from damp air and disintegrates. For this reason it must be packed in air-tight containers, causing extra expense and trouble. Much of the difficulty can be prevented by mixing in a little ammonium sulfate. Lime saltpeter has one advantage, it can be completely made use of by the plant, so the soil is not contaminated by any residue of less valuable substances.

Calcium cyanamide, made by the second of these processes, is also used a great deal as a fertilizer. Calcium cyanamide slowly changes in the soil to a plant poison known as *dicyanamide*, and the latter gradually changes to ammonia and finally to nitric acid. It must be strewn on the fields some time before the sowing of seed. It cannot be used as a top dressing. Its poisonous properties can be made use of to eradicate various organisms in the soil dangerous to the growing plant. Gas-purifying mass is also used for this purpose. This is a lime which has been used to remove the impurities from illuminating gas, the sulfocyanides, ferrocyanides, sulfides, etc. All these are poisonous, but after oxidation are good fertilizers. Calcium carbide is also used for the same purpose, as is crude naphthalene. These agents must be spread on the fields a good time before planting.

In various aspects phosphorous fertilizers have properties opposite to nitrogen fertilizers. They generally consist of *apatite*, or calcium phosphate with a little calcium fluoride, or instead a compound of calcium phosphate and silica which occurs in *slag* may be used. All are very difficultly soluble or become so as soon as they come into contact with the lime present in the field. The slag phosphates are easily soluble, often deliquescent. Phosphate acts principally on the root system of the plants, while nitrogen fertilizers further the development of the aerial system. Phosphate speeds ripening while the nitrates retard this process. As a result of the difficult solubility of phosphates they are not easily washed from the soil by rain water. This was shown at Rothamsted where phosphate fertilizer was added to a plot of ground for fifty-five years, and the amount carried away by crops was determined. Thus the increase in soil phosphate content not carried away by water could be found. The figures after the fifty-five years of use indicated that no notable washing away of phosphate had occurred. There is reason to believe that the mechanism of taking up of phosphates by plants is as follows: Carbonic acid in the soil frees a very slight amount of

phosphoric acid from the phosphates and an easily soluble mono-calcium phosphate is formed which is taken up by the roots of the plants. Phosphate is particularly valuable as an aid to binding nitrates in the earth for it is beneficial to the nitrite and nitrate bacteria, and also for the growth of the root systems of legumes.

Phosphates are found as mineral in many regions. The phosphates of Florida are best known. These contain about 80% tri-calcium-phosphate. Three molecules of lime are combined with two of phosphoric acid. This mineral can be directly strewn on the soil in pulverized condition. The natural phosphates act slowly because of their difficult solubility. Commonly therefore they are converted into *super-phosphate.* In finely powdered condition they are treated with sulfuric acid which combines with two-thirds of the calcium of the tri-calcium-phosphate and leaves a mono-phosphate, one molecule of lime to two of phosphoric acid, while calcium sulfate, *gypsum*, is also formed. The mass is dried and mixed with some finely powdered triphosphate which prevents the grains from lumping in moist air. The superphosphate must be kept dry till strewn on the fields, when it dissolves and seeps into the earth, to be changed back into the insoluble salt by the lime of the soil. If lime is not available in the soil, this salt will combine with iron oxide and form an extremely insoluble product — an end not to be desired. But when lime is present the phosphate becomes distributed evenly in the upper soil. Carbon dioxide in the soil can rapidly make it soluble again for use by the plant. So it acts quickly and can be used as a good top dressing. Sometimes lime is added with it to hold it in the top soil. *Bone ash* is similarly used; it also consists of tri-calcium-phosphate. It acts more slowly and does not make a good top dressing.

Thomas slag is obtained in the basic process of manufacture of cast iron. It may contain up to 40% of tri-calcium-phosphate. It also contains an equal amount of calcium in excess, together with up to 10% of iron oxide and a smaller quantity

of magnesia and of manganese oxide and calcium silicate. All these bodies are advantageous to plant life. Thomas slag is an excellent fertilizer if ground very fine. It is therefore sifted through a sieve of 0.25 mm. mesh. It is of particular usefulness on heavy clay or peat soils. It is less useful on sandy soil. The maximum effect is obtained two years after it is added to a soil.

Bone meal is a mixed, nitrogen and phosphorus fertilizer. Bone contains 44% of tri-calcium-phosphate, 28% nitrogen compounds, 10% fat and 5% calcium carbonate, the remainder being water with traces of magnesium and fluorine. It dissolves very slowly and appears nearly useless for plants. Its effects are greater if it is fine-ground, but is still better if the fat is removed. This is extracted with petroleum ether. The bone then becomes porous and can more easily be ground to a powder which dissolves fairly rapidly in the presence of the carbon dioxide of the soil. If the bone is boiled under high pressure, so that not only the fat but most of the glue-substances are removed, it becomes still more useful. Bone meal has much the same effect as has Thomas slag. The organic substances contained in the bone meal promote the bacterial flora of the soil. Among the mixed nitrogen and phosphorus fertilizers belong the various types of guano. Often they also contain a little potassium. They are highly prized as fertilizers.

Today nearly all potash comes from the salt deposits of Germany and Alsace. The latter are of the Tertiary period, the former from an older formation. The commonest potash salt is *kainite*, KCl with $MgSO_4$ and $3H_2O$. The potash content is 19% K_2O. The salt used in trade under this name actually contains only 12.5% K_2O. It contains much common salt and a little magnesium sulfate. The potash salt most abundant in the Germany deposits is *carnallite*, containing 17% K_2O. Before the war this was not exported. Kainite is very hygroscopic becoming lumpy in moist air, so it is commonly mixed with some dry powder to lessen this.

The potash salts added to a soil combine with calcium carbonate forming potassium carbonate, which becomes bound to the clay or to humus. The sulfate and chloride ions combine with the calcium and are washed away by water. The potash is held by the soil about as well as are the nitrogen and the phosphate. Experiments at Rothamsted show that in fifty years about one-quarter is lost.

The world consumption of potash before the war was about 1,100,000 tons per annum. The German deposits, according to Matignon contain about 7500 times this amount, the Alsatian deposits only about 300 times. The potash salts present in the Mediterranean Sea, could we use them, would furnish potash at the above rate for 900,000 years. During the war when the German supply was cut off there was anxious search for potash. In an old Roman salt mine at Cardona, potash was found in considerable amount. In Sicily it has been found. Very recently great deposits are said to have been discovered in the southwestern part of the United States.

During the war it was attempted in America to recover potash from cement furnaces, and also to gain potash from certain sea algae which were dredged up and burned. But these methods could not replace the lack of the German material. In 1910–1913 the import of potash into the United States from Germany was about 270,000 short tons per year. In 1914 this sank to 207,000 tons. In 1917, 3100 tons were imported, of which 17% came from Russia, 15% from England, 14% from Japan, 12% from Chili, 11% from Spain, 10% from Italy, 9% from France, 5% from Portugal, 4% from the Argentine, and 3% from other lands. The demand was more than 260,000 tons. For meeting this demand, the United States itself produced only 32,573 tons, only one-eighth of the needed amount. In 1916 the inland production in America was only 9720 tons, not one-third of the production in the following year, 1917, given above. The United States production in that year came from the following sources: Potash from the salt-seas 20,652 tons; from alunite, 2402 tons; from cement dust, 1621

tons; from kelp, 3572 tons; from molasses, 2846 tons; from wood ashes, 621 tons; other sources, 859 tons. Of course the price increase was tremendous — from $66 per ton of K_2O in the German fertilizers of 1912–3 to $429 per ton in 1917, an increase of 6½ times.

Of great importance in connection with the activity of fertilizers is the depth to which they penetrate the soil. The nitrates go deepest, so these are most likely to be washed away. They must be used as a top dressing. The ammonium ion is bound by the soil and does not go deeper than about 6 centimeters. The potash ion goes a bit deeper. The phosphate ion of superphosphate is held at about 20 centimeters depth, the Thomas slag phosphate stays nearer the surface, and is only carried down a few centimeters by the rain water. Soluble amines like urea and asparagin may be found as far down as 25-30 centimeters. Soluble albuminoids go only half as far, and egg-albumin is filtered out at the surface. The amines and albuminoids enter the soil with stall-dung.

For decision as to which fertilizer is best to use on a given field a knowledge of the food-stuffs already present in the soil is needed. This may be obtained by an analysis of the soil, which can be made at any agricultural experiment station. The results of these analyses and the nutritional needs of the particular crop to be planted determine the nature of the fertilizer needed. The so-called minimal rule applies here. It was propounded by Liebig. It says that the crop depends upon that particular plant nutrient which is present in the soil in the least amount relative to the need. If this particular nutrient is increased, then the biggest crop is obtained. Increase of the other nutrients is not so important. Too much of many nutrients can be injurious; this is particularly true of those stuffs needed by the plant in only very small quantities.

In earlier times men were led by rather arbitrary rules. Manure was spread on a field until no more action from it was observed. Lime was useful, so fields were limed until it was evident that too much had been applied. Then they turned to

artificial fertilizers until the soil was impoverished in lime. The most important duty of agricultural chemistry today is to give advice for remedying difficulties which have arisen from biased, rule-of-thumb treatment of the fields. It is not too sanguine to hope that the yield of a cultivated soil in civilized lands can be brought at least to double by the rational use of fertilizers and agents for improving the soil. For a long time to come agriculture will remain the most important field of application of chemical science.

Chapter XV

HOUSEKEEPING WITH THE TREASURES OF NATURE

Up to the beginning of the war we lived in an age of feverish development. In each ten years time we used up as much good coal as constituted mankind's entire previous supply over a period of 100,000 years. Of many other raw materials the story was the same. For that reason voices were raised asking the question, "What will happen if we continue living in this way? Like insane wastrels, we spend that which we received in legacy from our fathers. Our descendants surely will censor us for having squandered their just birthright."

But the group who thought and spoke in this manner were few in number and they were soon silenced by the prevalent, boastful bluster about industrial conquest. A few scientific men, among them certain famous names such as Crookes and Van Hise, comprehended the need for conservation. None of them were of the "practical" business-man type. Statesmen failed to understand the scientific calculations of these prophets, for statesmen are only in exceptional cases interested in nature and science, confining their minds to politics, lightly leavened with a veneer of law and literature. They counted these warnings to be curiosities of no practical importance.

It must be admitted and with some satisfaction that signs of a comprehension of the waste which was being carried on by our modern conquistadors in the name of civilization *did* begin to be evident to a few people who held leading political positions. The terrible cruelties perpetrated in the Congo and in South America, forcing the natives to surrender the produce of their land to greedy trade, may still be recalled. They became the object of parlimentary debates and of political action. In America, where pirating and money-lust have per-

haps exercised greater destructive activity than elsewhere in the world in recent times, Theodore Roosevelt, the president, in the year 1908 called together all the state governors to a conference to discuss how long the natural wealth of each state could be counted upon. The conference recommended the establishment of state commissioners to make an inventory of natural wealth. A three-volumed report was published in 1909. In that year President Roosevelt invited Canada, Newfoundland and Mexico to send delegates for a discussion of this important question. The new conference advised the calling of an international conference, so President Roosevelt requested the different governments to send delegates to the Hague to discuss conservation of the natural wealth of the whole world. But Roosevelt did not get the backing of the American congress in this matter and his appeal to the nations failed.

War came and everything else was pushed aside. Now it is over and we stand contemplating the dismal ruins. We have learned by bitter experience what it means to be cut off from supplies of coal and metals. We have gained a presentiment of the desolation which may threaten our descendants in a couple of centuries in case we do not succeed very shortly in inaugurating a more sensible way of keeping house.

The natural treasures at the disposal of man are of two kinds, material wealth, and energy wealth. The first type occurs in limited amount in the earth and this we must conserve. The latter accrues to us from the sun and we cannot increase or diminish it in any known way. But we can make use of it as advantageously as possible. There is a more or less intermediate group between these two types. To this middle group belong those products which arise from the conversion of less valuable materials into useful objects as a result of the action of solar energy. The plant world is our agent in this transaction which includes the harvest of our grainfields and of other cultivated areas, as well as the treasury of the forest. In cases where regrowth is comparatively slow we must introduce a

more rational plan of housekeeping, with careful thought for the future.

However, by far the greater part of our wealth consists of various valuable minerals, together with coal. We have already taken a sort of inventory of mineral and coal resources in an earlier chapter. We know that the minerals which furnish the metals most useful in our daily life will be depleted at the present rate of use within the lapse of a few hundred years. This is particularly true of fossil fuels and of the most valuable types of iron ore, but copper, tin, lead and zinc ores are also fast disappearing. They will be used up before various other raw materials.

The case of petroleum is worst of all. The oil fields of Pennsylvania and New York and those of West Virginia, have already failed us. Only by continual discovery of new fields has it been possible to increase production at the raging pace demanded and characteristic of our civilization since the middle of the last century. It is plain that the new wells of California, Oklahoma, etc., will dry up as rapidly as did the old ones of Pennsylvania, and the United States will soon be without this important source of income. New oil fields of great area have been opened up from time to time in different parts of the world, most recently in Mexico, Persia and Mesopotamia, but these cannot last very long. When the question of the security of mankind's future is at stake a few thousand years is a very short space of time. In order to lengthen the time in which man shall have available a supply of petroleum, its use as a lubricant and for light, heat and power must be cut to a minimum. The use of ball-bearings, of electric light and of electric power and heat, and perhaps the use of alcohol as a motor fuel will all aid in this economy.

The coal question is also difficult. Soft coal may last us about one thousand years. Long before that time the coal deposits of England and of Europe will be depleted. The disappearance of coal will be a terrible loss to mankind. We must lessen the calamity by making the transition a slow one.

We must begin to decrease the waste of coal. We use up in transportation a half a ton of coal for each ton taken from the mines. One hopeful sign in America is the superpower project at present under consideration whereby coal will be turned into electric power at or near the mines and the energy transported with smaller losses. The entire Appalachian system and New England are to be made a unit for economic use of the natural energy wealth. The heat obtained by burning coal should be used to far greater advantage than it is today. Our engines are not of high efficiency. In America a mercury engine has been devised, giving much higher efficiency than the steam engine and using the expansive power of hot mercury vapor. But cost of installation of such units is much higher than the cost of a steam unit. In the future that most useful product of coal, coal tar, must be treated with greater care than is done today, or the dye-industries will be crippled. But above all the power of waterfalls must be used as extensively as possible and solar engines and wind motors can be put into operation in suitable districts.

Fuel materials are lost for all time when they are used. Metals on the other hand can be melted and used again for other purposes. This makes the case of the metal ores somewhat different. Ores of lead, zinc, tin and copper and the noble metals are most in danger. Half the zinc smelted is used for galvanizing iron. Tin is much used for the protective coating in tin plate. These metal coats are lost after one period of usefulness. There has been some success in recent years in recovering tin from tin plate by electrolysis. Much tin is lost in dyeworks in the form of mordant and much zinc is used and never regained as zinc white in paints. About one-third of all the lead used, also, is destined to be lost as lead white. These metals are likely to become more and more expensive and that rapidly. They must be substituted by other materials. It should be possible to use barium white and possibly titanium white. The great waste of ores being, however, in mining and refining. Such losses can be decreased, and

nearly double the present yields can be obtained, especially of lead and zinc.

Copper is used mainly for electric machinery and conductors. In the latter use it can be replaced to advantage by aluminum just as it has been replaced by that same metal for kitchen utensils. Objects of copper are not lost, for the copper can be regained. The price of copper is so high that ores which were not formerly used on account of their low content of the metal are being worked up.

The noble metals are used chiefly for coinage. This continually wears away in use, so part of the metal is lost. The introduction of paper currency improves this situation. In America gold coins now rarely pass in circulation. The noble metals are also used a good deal for the manufacture of objects of ornament, and as a coating for less valuable metals. The former are rarely lost, but the gilding and silvering is rarely recovered. Silver and gold salts are used technically, especially in photography, in chemical practice, and in medicine. Only a very small amount of the silver and gold used in this way can be saved. Great reserves of gold and silver ores exist, of too low value to be worked today. It is fortunate that these metals are conserved to such an extent in treasuries and not wasted.

Silver is used considerably in industry, and it must increase in price some day as compared with gold. Signs of this are already evident. Platinum also belongs with the noble metals. This metal is in great demand as a catalyst in the contact process. Its use for jewelry was prohibited in many countries during the war. The expensiveness of platinum is a constantly irritating fact to the chemist, for it is of great use in the laboratory on account of its resistance to attack by chemicals. Gold is sometimes used in the laboratory in its place, and various alloys such as *ilium*, consisting of 60% nickel, 31% chromium, 2% each of copper and tungsten and 1% each of aluminium, silicon, manganese and iron.

Incomparably the most important of all metals is iron. The inventory made by the International Geological Congress at

Stockholm in 1910 cast for it an unfavorable horoscope. But man will be forced some day to economize in the use and working of ores. Iron objects will be coated with protecting layers of enamel and paint. Iron scrap is already carefully saved and used for the preparation of high quality steel in the electric furnace. Furthermore, we must replace iron by aluminium alloys in construction work, and we are today replacing much iron by cement in our building.

In spite of all the white books and explanations of the whys and wherefores of the world-war, hunger for iron and coal was undoubtedly a great contributing factor. The German geologists and manufacturers continually stressed as a live question for Germany the need to acquire the great minette ore-fields of Lothringen and the coal mines of Belgium and Poland. They were to aid Germany to dominate the world. On the other hand the peace terms gave a true expression of Allied war-aims for all important ore and coal fields were taken away from Germany.

The metal of the future is aluminium. Formerly it was made almost wholly from bauxite. A method was developed by Buchner in Germany during the war for preparing aluminium from kaolin or from clays rich in kaolin. Victor Goldschmidt in Christiania has devised a process for preparing aluminium from labradorite, so this may also become a valuable source. Aluminium forms some very valuable alloys, particularly with magnesium. There is little danger that the raw materials of these metals will ever be used up.

The materials for the ceramic and glass industries, quartz and silicates, compose 60% of the earth's crust. No fear that these shall ever be used up! Of the remaining raw materials we need not worry about lime and common salt. But the case of the potash salts is rather different, for their use has increased as rapidly as that of iron and coal. There is no immaterial amount of potash present in the earth's crust in felspars and other minerals, but to gain a soluble potash salt from these sources is difficult. At their present rate of use it is possible

that the potash salt deposits may last us about 10,000 years. If the rate increases in any large degree then we may have cause to fear their depletion. However, deposits are likely to be found in parts of the world not yet fully explored.

The phosphate deposits of Florida and South Carolina are not inexhaustible. Poorer grade material occurs widely scattered over the whole world, and can be used if the United States some day forbids export of her phosphate supply, as is likely. Little phosphate is really lost in agriculture, much remains in the upper soil layers, and even the part removed with the crop ultimately goes back to the fields again. The same is more or less true of potash.

The third type of fertilizers, the nitrogen compounds, formerly were the cause of much worry, for the Chili saltpeter deposits could not last more than a few decades, and even counting in poorer grade deposits a century would have seen the end of them. But now the chemist has succeeded in subduing the nitrogen of the air, and all fears of nitrogen-want have disappeared.

Soda, chlorine and chloride of lime are on the same basis as common salt. It will always be possible to prepare these important chemicals. Among the most important of non-metallic raw materials is sulfur from which is made sulfuric acid and the sulfurous acid used in the cellulose industries. Sulfur is found native in nature, in Sicily, in Louisiana, and in volcanic regions all over the earth. Pyrite can also be used as a source of it and this occurs widely scattered in nature. Even if this source should be used up, sulfuric acid could be made from gypsum by roasting it with the still more abundant mineral, quartz. The hydrogen needed in all acids is found present in water, oxygen we can always get from water or air.

Summarizing our inventory we can safely say that it is only fossil coal, together with petroleum and natural gas, which are destined to cause us serious anxiety. One might hazard the guess that coal and petroleum-producing lands will some day find it expedient to forbid export of these materials, or at

the least to set upon them a high export duty. Before the time of need arrives it is highly desirable that international agreements in this matter shall be arrived at. The greatest incentive to conservation will always be the pressure of necessity. The circumstance of iron ore is somewhat similar, as is that of copper, lead, tin and zinc ores. Precautionary measures must be taken in good season to prevent any great disturbance, due to their failure. A check can certainly be placed on plunder and on a heedless appetite for profits.

Concerning the intermediate group, the production of foodstuffs must be increased in every way possible. Dry areas must be irrigated, as has been done so widely in America, yet in this procedure certain precautions must be noted. In such areas the earth, with the exception of the uppermost soil layers, is often saturated with salts, generally of an alkaline nature. If water seeps down from the surface and dissolves these they may ruin the possibility of cultivation. A number of unfortunate attempts in Australia and in America have failed for this reason. Too much irrigation on the other hand has been known to change low-lying areas into swamps. The Yakama valley in Washington state was first a desert, because of the deficient rainfall. It was changed to a fruitful region by irrigation, and finally it was completely ruined by too much irrigation.

The dyking and draining of marshes is often of the greatest use for gaining tillable land, or for producing fine forest growths. The greatest undertaking of the sort occurred in Holland where a fertile land which was formerly the Haarlem Sea is now kept dry by continual pumping. It lies below the level of the sea. Plans are under way to regain some fruitful provinces in the Zuyder Zee region. These were ruined by the inroad of the ocean in the Middle Ages (1219–1287) and lie under water.

Yet precaution is always advisable. Draining and ditching lessen the evaporation of water, which would return to the fields as rain. The run-off is often extremely rapid, causing floods and lessening the even-flow of water needed for working water

powers. Homén in Helsingfors has emphasized the peril of unrestricted ditching and drainage of land, though this process was once considered particularly commendable.

Fields must also be kept in good cultivation and not let lie fallow. After a period of disuse much time and work is needed to return the land to full production. Legislation can help to prevent the spreading of new weeds. The formerly flourishing pastures of New England are today half covered with weeds, among which the Canada thistle is especially pernicious.

Forests are always important and continually valuable. Once it was considered good practice to clear a forest by burning it, in order to sow seed after a few years in the burnt-land. There is nothing more horrible than a forest over which fire has passed. A few naked, blackened skeletons of old trees still stand in the waste. But even greater damage has been caused by slashings and cuttings. Afterwards the rain waters run off much more quickly and cause floods; finally the rainfall is lessened and the drainage streams dry up. Many areas in the Mediterranean lands once fertile and densely populated have been changed in this way into unfruitful deserts. Such areas in Sweden and Denmark, once fine forest land, have changed to heaths unserviceable for cultivation, or near the coast to bleak headlands and sand dunes. Large areas on the Michigan peninsula in America are such wastes, and the cuttings in the Cœur d'Alene and other tracts in the Pacific Northwest bid fair to ruin another extensive area. At great cost and labor forests may be regrown on such tracts. But it takes a long time before the injury caused by the profit-seeking of industry, or by the fever of war with its program of boat-building, can be made good. The clearing of the forests in the United States merits anxious thought. For the rescue of the natural treasury jeopardized by waste and by careless treatment of the forests and crops, state intervention and control are most seriously needed.

What of the energy-treasury? This originates ultimately from the sun. Any notable change in our sunlight is not likely to occur. Such a change would bring about great climatic

disturbances. Extensive drainage and cutting off of forests may lessen precipitation slightly, but the effect cannot be very great. Thus mankind's influence upon solar radiation would not noticeably affect the power which could be gained from solar engines. Nor can man change the strength of the wind. It is possible that a great increase in carbon dioxide content of the air, due to burning of the fossil fuels, might bring about increased heat-absorption in upper-air layers and as a result lessen the temperature differences between different areas of the earth. This would lessen the strength of the wind, and the effectiveness of wind motors, but even if mankind united in working for it, no greater change is liable to be brought about.

The most important activity of the sun's rays in supplying us with useful energy, aside from that which is gathered in vegetation, is that energy which may be gained from waterfalls. The solar source of power, and the precipitation of water on the face of the earth can scarcely be increased or decreased. But the effectiveness of their use can be varied widely. We must seek to equalize the flow of the streams and try to make them nearly unchanging in volume throughout the year. For this purpose lakes or reservoirs to impound the water must be made by building dams, taking care not to inundate useful land. The drainage basin of a water power should not be ditched or cleared of forest, for such operations are equal to lessening the water reserve. Unlike fossil fuel these sources of power are not depleted by use. Lands which have much of this form of natural wealth may consider themselves lucky.

There holds in chemistry a rule which must be applied in all wise housekeeping. It is the "Chemist's Commandment."

"*Thou shalt not waste.*"

Thou shalt not destroy anything useful. It is the use of so-called waste products which brings about a maximum return. Herein lies our hope for the future. Priceless is that forethought which has lifted mankind from the wild beast to the high standpoint of civilized humanity.

INDEX

A

Abbe, 102, 103
Abraum-salz, 153
Acetic acid, 7, 195–196, 203, 207, 239
Acetone, 239
Acetylene, 136
Acetyl-salicylic acid, 230
Acheson, 193
Achromatism, 101
Acids, 12, 14, 26, 112, 177, 198, 204, 207
Ackermann, 170
Adrenaline, 236
Affinity, 22
Age of earth, 123–126
Agglutinin, 206
Agricola, 9, 62
Alberuni, 7
Albiez, 214
Alchemy, 6, 7, 11, 31, 32, 65
Alexandrian school, 17
Algae, 122
Algol dyes, 222
Ali ben Isa, 229
Alizarin, 219
Alkali, 13, 26, 83, 242
Alkali metals, 83
Alloys, 64–82
Alumina, 55
Aluminum, 33, 54–56, 81–82, 272
Aluminum brass, 76
Aluminum bronze, 76
Aluminum silicates, 99
Aluminothermy, 55
Alypin, 229
Amalgam, 78
Amino acids, 253–255
Ammonia, 133, 217–218
Ammonium carbonate, 217–218
Ammonium chloride, 88, 217
Ammonium sulfate, 133, 140, 260
Amphibole, 98
Amygdaloid, 242
Amyl acetate, 228
Amyl isovaleriarate, 228
Amyl salicylate, 228
Amyloid, 242
Anaemia, 234
Anaesthetics, 229
Anaximenes, 2
Andalusite, 99
Anethole, 227
Anilin, 216
Anode, 181
Anthracene, 219, 222
Anthracite, 130–133
Antifebrin, 230
Antimony, 79, 129, 187
Antipyrin, 230
Antiseptics, 229, 235–236
Antitoxins, 204, 236
Apatite, 261
Apple essence, 228
Arabic chemistry, 7, 9
Archimedes, 3, 17, 22
Argon, 4, 5, 18, 156
Aristotle, 2, 4, 5, 19
Arrhenius, x, xi, 177, 199, 204–205, 236
Arsenic, 5, 10, 234–235
Arsphenamine, 235
Art bronze, 74
Artificial fertilizers, 259–266
Artificial silk, 242–246
Asparagine, 265
Aspden, 106
Asphalt, 136, 137, 142
Aspirin, 230
Astrology, 12, 31
Atmosphere, 156–159
Atomic theory, 27, 28, 30, 32
Atomic weights, 29, 32–34
Atoms, 5, 19, 27–30
Atoxyl, 234
Aventurine glass, 105
Avogadro, 30–31, 196–198, 201
Azo dyes, 222

B

Bacon, of Verulam, 18
Bacon, Roger, 6
Bacteria, 159, 257–258
Baeyer, 220
Baker, 212
Baly, 253
Banting and Best, 236
Barium, 57, 122, 270

Barrett and Brown, 67, 70
Baudin, 101
Bauxite, 82, 116
Bayer, 205, 235
Bearing metal, 74
Béchamp, 234
Becher, 20
Becker, 155
Bell metal, 74
Benedicks, 70
Benzidine dyes, 222
Benzolicht dyes, 222
Benzol, 136–137, 214
Bergman, 21-22
Berlin blue, 179
Berthelot, D., 252
Berthelot, M., 6, 161, 296
Berthelot and St. Gilles, 202
Berthollet, 36
Berzelius, 29–32, 35, 176, 206, 256
Bessemer process, 66
Bevan, 244
Birkland and Eyde process, 202, 260
Bismuth, 79–80
Bjerrum, 201
Bleaches, 57, 192
Blood, 20, 24–25, 206, 226
Blumenthal, 234
Boeke, 122
Boerhave, 20
Bohemian glass, 99
Bohn, 222
Bonding of cement, 108, 109
Bone ash, 93, 262
Bone meal, 263
Bone, W. A., 49
Borax, 92, 154–156
Boric acid, 101,113, 156
Böttger, 44
Bottle glass, 100
Bourquelot, 205
Boussingault, 256, 257
Boyle, 12, 18, 19, 43
Boyle's law, 19
Boys, Vernon, 100
Brahe, Tycho, 18
Brahma, 1
Brand, 23, 43
Brandenberger, 289
Brandt, 23
Brass, 76
Brauer, 210
Breathing, 24–25, 52–53
Breccia, 119
Bredig, 199, 207
Bridel, 205
Britania metal, 79
Brown, 67, 70
Bromine, 155, 192, 197
Bromoform, 232
Bronze, 61, 73–77
Bronze age, 62, 73
Brun, 112
Brundusium, 74
Brüstlein, 67
Buchanan, 147
Buchner, 252, 272
Buffon, 12
Bunsen, 112, 184
Bunsen's cell, 184, 190
Bureau of Standards, 107
Burgess and Aston, 70
Butadiene, 248

C

Cadmiun, 80
Caffein,231
Cahen, 45
Cahn and Hepp, 230
Calc, 23
Calcium carbide, 193, 261
Calcium carbonate, 145–146
Calcium cyanamide, 193, 261
Calcium phosphate, 43, 261–262
Calcium silicate, 98
Calcium sulfite, 239
Callaud's cell, 185
Camphor, 228
Cannizzaro, 31
Carbides, 136–137
Carborundum, 193
Carlisle, 176
Carnellite, 263
Caro, 260
Carrel and Dakin, 235
Cassiterite, 129
Cast iron, 65–66
Catalysts, 206–212
Cato, 256
Cavendish, 21, 25
Cellite, 245–246
Cells, electric, 184
Celluloid, 241
Cellulose, 137, 237–247
Cellulose acetate, 245–246
Cellulose nitrate, 240–241
Cellulose xanthate, 243–244
Cement, 98, 105–110, 264

Cement copper, 26
Cement kiln, 106–108
Cerium, 40–41
Challenger expedition, 145
Chancel, 42
Chardonnet, 244
Chelles-time, 59
Chemical formulas, 35
Chemical industry, 216–218
Chemical lighter, 42
Chemical symbols, 32–35
Chevenard, 70
Chevreul, 254
Chili saltpeter, 214, 260, 273
Chinese chemistry, 10, 25
Chladni, 111
Chloral hydrate, 229
Chloride of lime, 57, 192, 212, 217, 228, 229, 273
Chlorination, 57
Chlorine, 57, 192, 212, 216–217, 221, 229, 273
Chloroform, 229
Chlorophyll, 252
Chrome steel, 55, 72
Chromium, 55
Clarke cell, 188
Clarke, F. W., 33, 114, 131
Claude, 202
Clay, 85–88
Coal, 130–143
Coal tar dyes, 222
Cocain, 232
Cohn, 121
Collodion, 141
Colored glass, 105
Columella, 256
Common salt, 149, 150
Conductivity, 181–184
Conglomerate, 119
Congreve's striker-sticks, 42
Conservation, x, 137, 142–143
Contact metamorphosis, 1
Contact process, 209
Copper, 61, 73–77, 270–271
Copper oxide ammonia, 243
Copper sulfate, 26
Coral reefs, 121
Cordite, 240
Cordus, 206
Corubin, 55
Cotton, 215, 240
Coutelle, 248
Creation, 1–2
Crofts, 196–197
Cronstedt, 23
Crookes, 267
Cross and Bevan, 244
Crown glass, 101
Crystal glass, 99
Crystobalite, 89, 91
Culture, 37, 59–62, 85–86, 94–97, 226–227
Cupron cell, 185
Curie, 68
Cyanamide process, 260

D

Dalton, 27–29, 34
Daniell's cell, 185
Darwin, 59
Da Vinci, Leonardo, 17, 24
Davy, 48, 83–84, 176, 193, 256
Day and Sheperd, 112–114
Dead Sea, 154–155
Debray, 199
Decay, 53
Deimann, 175
De la Boe Sylvius, 8
Delta metal, 81
Democritus, 4, 5, 19, 28
Derosne, 43
De Saussure, 256
Deville, 55, 200
Dextrin, 254
Diamond, 134
Dibromindigo, 221
Diffusion, 151, 185
Dimethylbutadiene, 248
Diptheria, antitoxin, 204
toxin, 204
Disinfection agents, 192, 235
Dissociation, Degree of, 30, 182–183, 195–203
Disthene, 99
Dittmar, 148–149
Diuretics, 231
Dixon and Baker, 272
Döbereiner, 41
Doelter, 128
Dolomite, 122
Drake, 141
Drugs, 228–236
Duclaux, 252
Dulloa, 23
Dulong and Thenard, 48
Dyes, 219–226
Dynamite, 240

E

Earth density, 111
Ebonite, 247
Edison, 187
Edison cell, 187
Egyptians, 6, 77
Ehrlich, 234–235
Eichengrün, 246
Einhorn, 232
Einhoven, 100
Ekman, 238
Elasticity, 70–72, 247
Electric current, 58
Electric light, 193
Electrification, 270
Electrochemistry, 190–194
Electrolytic-refining, 171
Electron, 178
Electromotive force, 176, 188–190
Electroplating, 191
Elektron (alloy) 77
Element, 1–4, 31–43
Empedocles, 5, 24
Emulsion, 205
Energy, 160–174
Engler, 137
Enzyme, 203, 205, 207, 255
Equilibrium, 35, 36
Ericsson, 170
Erythrite, 243
Erosion, 114–119
Ester formation, 202–203, 207
Ether, 229
Ethyl acetate, 202–203, 207–228
Ethyl alcohol, 202–203, 207, 239, 255
Ethyl ether, 229
Ethyl sulfuric acid, 229
Ethylene, 27-28
Euclid, 169
Eudiometer, 21–22
Explosives, 240,241
Eyde, 201, 260

F

Faïence, 90–92
Faraday, 48, 69, 176
Fat, 203, 253, 263
Fatty acid, 203
Felspar, 90–91, 93, 99, 109, 114
Ferment, 205
Ferrosilicon, 66
Film, 242, 246
Fire, 2, 3, 11, 59
Fire damp, 134
Fire making, 37–43
Firestone, 39
Firing-point, 46–47
Fischer, Emil, 224, 231–232, 253–254
Flame, 11, 45–46
Flashlight, 55
Flint, 39, 59–60, 120
Flint and steel, 39
Flint glass, 101
Fluorescein, 223–224
Fluorides, 100, 129
Fluorine, 100
Fluorite, 129
Formaldehyde, 252–253
Foucault currents, 67
Four elements, 1, 2, 11
Frank, 257, 260
French glass, 99
Friedländer, 221–222
Fritt-porcelain, 92
Fuchsin, 223
Fuels, 130–143
Fumaroles, 112, 155–156
Fürstenburg, 41

G

Gahn, 23
Galvanoplastics, 191
Gas laws, 27, 29, 199
Gassendi, 19
Gaudechon, 252
Gautier, 113
Gay Lussac, 27–30
Geber, 209, 214
Geologic thermometer, 151
Geophysical laboratory, 104, 107
German silver, 75
Glaciers, 114, 117
Gilbert, 257
Glanzstoff, 244
Glass, 94–105
Glauber, 9
Glauberite, 151
Glauconite, 88
Glazes, 90, 92
Globigerina, 146
Glucose, 254
Glucosides, 205
Glycerine, 192, 203, 229, 243, 253, 253 254
Gneiss, 113
Gold, 77–78, 271
Goldschmidt, H., 54–55

Goldschmidt, V., 272
Gorgjanovic, 59
Gräbe and Liebermann, 219
Graham, 48
Gram calory, 160
Gram equivalent, 182–183, 189
Granite, 113
Grape sugar, 254
Graphite, 66, 123, 133–134, 193
Gray iron, 66
Great war, v, 104, 139
Greek-fire, 213
Green, 222
Grenet's cell, 184
Griess, 222
Grignard, 211
Guano, 263
Guericke, 19
Guertler, 70
Guilliaume, 70–71
Guldberg and Waage, 183–184, 203–208
Guncotton, 240
Gunpowder, 25, 56, 213
Gustav Vasa, 214
Guye, 34
Guyton de Morveau, 21
Gypsum, 87, 262

H

Haber process, 192, 202, 208–210, 260
Hadfield, 67–70
Haematite, 122
Haemoglobin, 205
Haemolysin, 205, 208
Half-crystal glass, 101
Hardening of fats, 211
Hardness, 22, 68, 72, 74–76, 81, 93, 101
Harries, 248
Harun al Rashid, 9
Hata, 234–235
Heat, 134, 160–164
Heimdall, 37
Helier, 48
Heliotropin, 227–228, 231
Helium, 123–125, 156
Hellreigel and Willfarth, 257
Helmholtz, 189–190
Helmholtz cell, 188
Henderson, 67
Henriques, 255
Hepp, 230
Heraklitus, 2
Hermann, 95
Hero of Alexandria, 169
Heroult, 272
Hiero of Syracuse, 17
Hindu Chemistry, 6–10
Hippocrates, 7
Hittorf, 181
Hjärne, 11–16
Hoffman, 216, 248
Högbom, 122
Holmes and Lawson, 124–125
Homberg, 22
Homén, 275
Hopkinson, 69–70
Hornblende, 114–116
Horsepower, 164–166
Horstmann, 198
Humoral-pathology, 7
Humus, 256
Humic acid, 47, 136
Hyatt, 241
Hydrastinin, 231
Hydroelectric power, 164–168
Hydrogenation, 58
Hydrolysis, 205, 255
Hydroxyl, 177, 180
Hygiene, 235
Hypnotics, *see* Soporifics
Hypochlorite, 57, 192
Hysteresis, 67

I

Iatrochemistry, 8–10
Igneous rock, 114
Illium, 271
Indanthrenes, 222
Indicators, 225–226
Indigo, 259–261
Insulin, 236
Invar, 71
Invertase, 208
Iodine, 196–197
Iodoform, 229
Ions, 176–184
Ion theory, 177–184
Ionone, 227
Iridescent glass, 105
Iron, 61–73, 145, 271–272
Iron-cap, 130
Iron ore, 63–65, 122, 127–130
Irvine, 145
Isatis tinctoria, 220
Isoprene, 248

J

Jackson and Warren, 229
Jet, 132
Joly, 124
Julien metal, 187
Jungner, 187
Juvenile water, 128–129

K

Kainite, 263
Kammerer, 43
Kaolin, 87, 89, 117, 272
Kaplan, 165
Karaboghas bay, 152–153
Keyland, 38–40
Kieserite, 151
Klaproth, 25
Klingenstierna, 10
Knorr, 230
Koch, 234
Koehn and Kaplan, 165
Ko-Hung, 10
Kolbe, 230
Kramberg-Gorgjanovic, 59
Krypton, 156
Kunkel, 15

L

Labradorite, 272
La Cour, 171
La Fontaine, 11
Lagerman, 54
Langbeinite, 151
Laterite, 116–117
Lava, 114
Lavoisier, 23, 24
Law, of Faraday, 176–177
  mass action, 183–184, 195–199
  multiple proportions, 29
  Planck, 199
  van't Hoff, 199, 200
Lawes and Gilbert, 256–257
Lawson, 124, 125
Lead, 78–79, 124–125, 270
Lead chamber process, 215
Lead glass, 101–102
Lead storage battery, 186–187
Lead superoxide, 187
Lead white, 270
Leblanc, 83, 215, 216
LeChatelier, 88–89, 120, 207
Lechlanché's cell, 184
Lémery, 12–13, 20
Lenses, 102
Lepsius, 115
Libavius, 8
Liebermann, 219
Liebig, 229, 256, 265
Liebreich, 229
Life elixir, 7–8, 10
Lignin, 131
Lignites, 132, 138
Lime saltpeter, 260
Limestone, 120–122, 145–146
Limonite, 122
Lipase, 203, 211
Lithosphere, 33
Litmus, 180, 225
Loess, 117, 118
Loewite, 151
Lucretius, 24
Luminal, 232
Lundén, 205

M

Madsen, 204, 208
Magmas, 112–114, 128
Magnalium, 82
Magnesium, 55, 57, 82, 146, 251
Magnetism, 68–70
Malaguti, 203
Malaria, 235
Malleable iron, 66
Manganese, 65, 67, 70
Manganese steel, 67
Mankh, 9
Mansur, 9
Mao Koa, 25
Marcasite, 51, 53
Margarine, 254
Marggraf, 22, 203
Mass action, 183–184
Matches, 42–45
Matignon, 264
Mauve, 216
Maynard, 241
Mayow, 20, 25
Meade, 106, 108
Medical chemistry, 6–8
Meidinger, 185
Meisenheimer, 252
Melting point of metals, 79–80
Mendel, 255
Mendelejeff, 136
Menthol, 227
Mercer, 243
Mercerization, 243

Mercaptan, 233
Mercury (*see also* Quicksilver), 78, 211, 220
Mesotan, 231
Metals, 61–84
Meteorites, 34, 111
Methane, 133–136
Methanol, 239
Methyl salicylate, 230
Methyl violet, 211
Meyer, 169
Meyer and Crafts, 196–197
Microörganisms, 132–134, 156
Minette ores, 127
Ming dynasty, 93
Mirror metal, 74
Mitscherlich, 238
Moissan, 137
Molecule, 30
Molybdenum, 73
Morgenroth, 235
Morphine, 233
Mouchat, 169
Müller, 116
Murray, 118
Muspratt, 215

N

Naphthalene, 135, 211, 219–220
Narcotics, *see* Soporifics
Natural gas, 136
Natural resources, vi, 267, 376
Neo-arsphenamine, 235
Neolithic time, 60
Neon, 156
Nephelene-syenite, 98
Nernst, 200–201, 225
Neutralization, 27
Nicholson and Carlisle, 176
Nickel, 69, 211
Nickelin, 75
Nickel steel, 69–72
Nickel storage battery, 187–188
Nikolaus, 229
Nitrate bacteria, 257
Nitrate deposits, 156
Nitrates, 156, 259–260, 273
Nitrite bacteria, 257
Nitrobenzol, 227
Nitrocellulose, 240, 245
Nitroglycerine, 240
Nitrogen fixation, 156
Nobel, 226, 241
Nordenskiöld, 61
Normal cell, 188–189
Novocain, 232

O

Obsidian, 60
Oils, 58
Oils, essential, 227
Olefines, 135, 137
Oleic acid, 58, 211, 253
Oligoclase, 116
Olivene, 116
Optical instruments, 72, 102, 103
Optochin, 235
Ore, 127–130
Ormuzd, 1
Osborn, 59
Osborne, 255
Osiris, 79
Osmund and Weiss, 70
Ostwald, 183, 204, 207, 210
Oxalic acid, 239
Oxidation, 46–54
Ozone, 47, 56, 157

P

Paets van Trovstwyk, 175
Pakfong, 75
Paleolithic time, 59–61, 85
Palissy, 9, 256
Palmitic acid, 253
Pandermite, 92
Paper, 238–240
Paper pulp, 238
Paracelsus, 8, 9, 12, 81
Paraffine, 135
Parchment paper, 242
Partington, 238
Pasteur Institute, 235
Péan de St. Gilles, 202
Peat, 132
Perfumes, 227–228
Pergamoid, 241
Peridote, 99
Perkin, 216, 222
Petroleum, 130, 140–143, 269
Petunze, 94
Pharmaceutical chemistry, 228–236
Phenacetin, 230
Phenol, 216, 219, 223, 227, 230
Phenolphthalein, 224
Philosopher's wool, 81
Phlogiston, 20, 25–26
Phosphates, 259–263, 273
Phosphine, 47

Phosphor bronze, 75
Phosphorus, 43, 47, 157, 251
Phosphorus matches, 43
Phosphorus, red, 44
Phthalic acid, 211, 220
Planck, 199
Planté, 186
Platinite, 72
Platinum, 48, 209–210, 271
Plato, 3, 4
Pleochroism, 124
Pliny, 221, 256
Plutonic rock, 114–115
Pneumatic lighter, 41
Polarized light, 137
Polymerization, 248, 252
Porcelains, 91–94
Porosity, 49–89
Portland cement, 106
Potash, 109–110, 263, 272–273
Potash salts, 153–154
Potassium, 83
Potassium chlorate, 58
Potassium permanganate, 57
Potassium silicate, 98
Pottery, 58–90
Pozzuolana, 106
Precision glass, 104
Preschel, 44
Priestley, 21, 23, 26, 52, 175, 229, 252
Principles, 12–13
Prometheus, 37
Protein, 251, 253, 255
Proust, 29
Pseudowollastonite, 98
Pteropods, 146
Puddingstone, 119
Purines, 231
Purple, royal, 221–222
Pyramidon, 230
Pyrex, 104
Pyrrol, 216

Q

Quartz, 100, 272
Quicksilver, 6, 7, 11–13
Quinine, 235

R

Radioactivity, 123–126
Radium, 124
Ramsay, 30
Ramus, 18
Rankin, 108
Rare gases, 156
Rasayana, 7
Ray, 7–8
Rayleigh, 124
Reaction speed, 209–212
Realgar, 10
Réamur, 65, 105
Recalescence, 68
Red clay, 118
Red phosphorus, 44
Reduction, 23, 54–58, 175
Religion, 6, 10, 40, 60
Residual torsion, 100
Resorcin, 223
Respiration, 24–25, 52–53
Reusch, 123
Rheumatism, 229
Richards, 24
Richter, 26
Riley, 69
Rinman, 67
Ritter, 175–176
Roebuck, 209
Rogers, S. B. and R. E., 116
Roman glass, 96
Rontgen rays, 103
Roosevelt, 268
Rose metal, 79
Ross, 110
Rubber, 247–249
Rubidium, 145
Ruer and Schütz, 68
Runge, 216,
Rusting, 54
Rutherford, 21

S

Sabatier, 58, 207, 211
Saccharimeter, 205
Safety matches, 44–45
Sainte Claire Deville, 55, 198
Sal acidum universale, 12
Salicylic acid, 230
Salt, 11–13, 148–150, 177
Salt deposits, 150–154, 217
Salt-graze, 90, 92
Saltpeter, 13, 213–214, 218
Salvarsan, 235
Sandstone, 119
Saussure, 256
Scheele, 21, 23, 42
Scheffer, 20
Schlossing, 145
Schmidt, 222

Schönbein, 240
Schott, 103–104
Schröder, 163
Schrötten, 44
Schungite, 133
Schützenberger, 245
Sea water, 144–146
Sederholm, 125
Sedimentary deposits, 122–123, 128
Serpentine, 99
Serrander, 167
Serullas, 229
Sèvene and Cahen, 45
Sèvres porcelain, 92
Shale, 120
Shen-Nung, 10
Sheperd, 112
Shists, 122–123
Shuman, 170
Sikoid, 246
Silicates, 85–100
Silicon, 33, 65–67, 76
Silicon bronze, 76–77
Silliman, 141
Sillimanite, 99–100
Silver, 61, 78, 271
Simpson, 229
Sjögren, 63
Slag, 66
Smeaton, 106
Soaps, 83, 192
Sobrero, 240
Soda deposits, 154, 155
Sodium, 57, 83
Sodium carbonate (soda), 83, 154–155, 213–218, 260, 273
Sodium silicate (water glass), 97–98
Sodium sulfate (Glauber's salt), 35, 83, 217, 238
Sodium sulfhydrate, 83, 238
Soil chemistry, 257–266
Solar engines, 169–173
Solar heat, 162–164, 172
Solder, 79
Solubility, 115–117, 144
Solvay, 216–218
Soporifics, 232–234
Sörensen, 225
Soubeiran, 228
Speed of transport, 181
Spirosal, 231
Stahl, 20
Stained glass, 96, 105
Stassfurt salts, 150–153
Stearic acid, 58, 211, 253
Steel, 62, 66
Steinmann, 121
Stodart, 69
Stoichiometry, 27
Stoklasa and Zdobnicky, 253
Stolz, 231
Stoneware, 92
Storage batteries, 173–174, 186–188
Storer, 137
Strass (paste), 102
Strehlenert, 239
Stromeyer, 80
Strontianite, 122
Strutt, 124
Sublimation, 7
Sugar, 254
Sulf-arsphenamine, 235
Sulfate pulp, 238
Sulfite pulp, 138
Sulfite spirit, 239
Sulfonal, 232
Sulfur, 11, 13, 16, 23, 34, 42, 66, 114, 136, 247, 273
Sulfuric acid, 35, 206–210
Sun, 34, 111, 157, 162
Superphosphate, 262
Surface combustion, 48–51
Svedberg, 165
Svedrup, 172
Sylvius, 8
Synthetic drugs, 228–236
Synthetic dyes, 219–226
Synthetic perfumes, 228
Synthetic rubber, 248
Syphilis, 235

T

Talc, 7
Tammann, 68, 70
Tang dynasty, 10
Taylor, 73, 203
Temperature, 30, 68–73, 75, 101, 183, 199–203, 208
Terpenes, 227
Tetronal, 232
Textile industry, 218
Thaer, 256
Thales, 2, 12
Thénard, 48
Theobromine, 231
Theophylline, 231
Thermit, 56
Thioindigo dyes, 222

Thomas, 234
Thomsen, 190–204
Thorpe, 8
Thuringer glass, 101
Tin, 61, 78, 79, 270
Tin-glaze, 90–92
Titanium, 56, 270
Toluol, 219
Tools, 59–61
Transmutation, 5–6, 65
Trevany, 42
Tridymite, 89, 99
Trional, 232
Trona, 155
Trypan red and blue, 235
Tschi-Hoang-Ti, 10
Tull, 256
Tungsten, 21, 55, 73, 80
Tungsten steel, 73
Type metal, 79

U

Uranium, 124
Usiglio, 150

V

Valentinus, 78
Van Helmont, 8, 11, 12, 18
Van Hise, 140, 143, 267
Van Marum, 175
Van't Hoff, 35, 150–151, 161, 196, 198, 199, 201–204
Van'thoffite, 151
Vedas, 1, 7
Verguin, 222
Veronal, 233–234
Virgilius, 256
Viscose, 244–246
Voelter, 238
Volcanic vapors, 112
Volta, 175–176, 184
Volta's cell, 184
Voltaic pile, 175–176
Von Pabal, 198
Von Wartenberg, 201
Von Wittenstrom, 67

W

Waage, 183–205
Walden, 133, 184
Walker, 43
Wallach, 227
Wallerius, 302
Wandering of ions, 180
Warren, 137, 229
Washburn and Weiland, 199
Water, 3, 22, 52, 112–118, 145–155
Waterglass, 97
Weiland, 199
Weiss, 70
Welding, 56
Wells, 229
Wenzel, 207
Weston cell, 189
White, 73
White-iron, 66
Whitney, 215
Willesden, 243
Willfarth, 257
Williamson, 206
Willis, 8
Wind-power, 171–172, 270
Winkler, 221
Winogradsky, 257
Wintergreen oil, 230
Witherite, 122
Wöhler, 44, 82
Wollastonite, 98
Wood's metal, 79

X

Xenon, 156

Y

Yang, 25
Yeast, 208, 225
Yin, 25
Young, 145

Z

Zarathustra, 1
Zdobnicky, 253
Zeiss, 102
Zeppelin metal, 82
Zinc, 81, 270
Zincblende, 128
Zinc chloride, 242–243
Zinc oxide, 81, 105
Zinc white, 270

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